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High Energy and Power Co-Continuous Electrodes Derived from Bijels

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High Energy and Power Co-Continuous Electrodes Derived from Bijels

DISSEDIATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemical and Biochemical Engineering

by

Jessica Ann Witt

Dissertation Committee:
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1. Co-continuous electrodes derived from bijels that simultaneously deliver high energy and power densities, J. A. Witt, D. R. Mumm, A. Mohraz (Submitted, 2015)

CONFERENCE PRESENTATIONS

1. High power and energy co-continuous electrodes derived from bijels, by J. A. Witt, D.R. Mumm and A. Mohraz, will be presented at the ACS Colloids and Surfaces Symposium, June 2015 Pittsburgh, PA.
ABSTRACT OF THE DISSERTATION

High Energy and Power Co-Continuous Electrodes Derived from Bijels

By

Jessica Ann Witt

Doctor of Philosophy in Chemical and Biochemical Engineering

University of California, Irvine, 2015

Professor Ali Mohraz, Chair

Next-generation energy storage materials aim to combine the best characteristics of batteries and supercapacitors, producing devices that concurrently deliver high energy and power densities. In order to achieve this goal, the kinetics of ion and electron transport within the electrodes must be enhanced while maintaining a large volume fraction of electrolytically active material for energy storage. In this regard, the idealized electrode microstructure has been envisioned as a three-dimensional, co-continuous arrangement of percolating domains that allow for large interfacial contact between the constituent phases and low-resistance paths for ion and electron transport. In this dissertation, I report a novel method to produce this unique microstructure through the use of soft matter templates derived from bicontinuous interfacially jammed emulsion gels (bijels). These non-equilibrium soft materials inherently have a co-continuous microstructure, where two interpenetrating fluid domains are kinetically arrested through jamming of particles at the fluid-fluid interface during spinodal decomposition. The neutrally-wetting colloids adsorb to the fluid interface upon phase separation and become jammed when the interfacial area is sufficiently reduced to just accommodate them. The characteristic domain size, which
establishes both the pore diameter and the internal surface area, is controlled solely through the overall colloid volume fraction and can be tuned over a wide range. Through simple chemical post processing steps, bijels are converted to electrolytically active composites. Combined, the morphological control afforded during bijel formation and our chemical processing steps allow for independent tailoring of the microstructural parameters that govern the electrode's electrochemical performance. In this work, I present composite electrodes that I have synthesized through this route and demonstrate how their salient electrochemical characteristics are dictated by these morphological parameters, allowing for concurrent delivery of high energy and power, bridging the gap between modern batteries and supercapacitors.
1. INTRODUCTION

1.1. MOTIVATION

Energy storage and conversion systems, such as batteries, supercapacitors and fuel cells, play an integral role in our everyday lives, since many of the electronic devices used daily, i.e. cell phones, laptops and remotes, rely on these technologies for power. Furthermore, the rising concern for fossil fuel dependency and determination for clean energy has provoked a worldwide resurgence in searching for alternative energy. These systems, such as wind, solar and hydro, require advanced electrical energy storage systems to manage the mismatch between energy generation and storage. However, it is widely understood that advances in these technologies are needed to meet the expected future energy demands\(^1\).

In areas such as microelectromechanical systems (MEMS), which are widely used as sensors and actuators in a variety of applications from ink-jet printers\(^2\) to medical implants\(^3\)-\(^5\), state of the art energy storage devices do not meet the current power and energy demands\(^6\). Considering that microprocessors follow Moore’s law, in which the performance of the device doubles every two years, but the most widely used energy storage system, Li-ion batteries, only exhibit a 10% increase in performance every year; there is a major discrepancy between these two technologies\(^7,8\). Thus, in many electronic devices, the overall size of the system is controlled by the volume in which the battery occupies\(^9\). Consequently, in order for increased miniaturization of these devices, there needs to be significant strides in the area of the amount of stored energy and power delivery per unit volume and mass.
These two performance measures are termed energy and power density. In particular, energy density is the amount of energy per unit mass or volume and power density is the rate of energy release per unit mass or volume. These are two of the most important performance characteristics for energy storage and conversion technologies and are typically depicted on a Ragone plot, as shown in Figure 1. Also as illustrated in Figure 1, in order to meet future energy and power demands, devices need to manufactured that concurrently deliver the high energy densities of batteries and the high power densities of supercapacitors. To achieve this goal, ion and electron transport within the system must be improved. This can be achieved through a wide variety of techniques, such as the discovery of new energy storage materials or electrolytes\textsuperscript{10-13}, improving upon the current set of materials\textsuperscript{14,15}, and through microstructural development\textsuperscript{16,17}. In particular, it has been proposed that through optimizing the manner in which material is arranged in an electrode
(especially in a three-dimensional arrangement), the electrochemical characteristics can be drastically improved\textsuperscript{18}. As such, the optimal electrode has been envisioned as interpenetrating, three-dimensional pathways for efficient electron and ion transport\textsuperscript{9}. Additionally, it has been suggested that an ideal electrode should satisfy the following three major criteria: it must contain a highly porous and interconnected backbone that acts as the current collector, the electrolytically active material must form a thin layer on the current collector, and the material must be free of organic binders\textsuperscript{19}. To date, there have been a handful of attempts to create this idealized electrode structure, via inverse colloidal templating\textsuperscript{20}, polymer scaffolds\textsuperscript{21}, nanofoams\textsuperscript{22}, and nanotubes\textsuperscript{23}. These initial strides have shown that a three-dimensional, co-continuous microstructure can achieve rapid charge and discharge rates while maintaining a high energy density\textsuperscript{20}. Further improvement on the idealized microstructure can be achieved by carefully designing the electrode’s structure through selecting a material that is inherently co-continuous. Microstructural design of the electrode not only allows for enhanced features, but can also allow for a more fundamental understanding of the role that the morphology plays in the overall performance of an energy storage device. In this dissertation, I utilize a relatively new class of soft materials termed bicontinuous interfacially jammed emulsion gels (bijels)\textsuperscript{24}, which inherently contain percolating paths of two co-continuous domains, as a template to create an idealized electrode microstructure and explore the effects of microstructural design on the electrochemical performance of electrodes.

The rest of the introduction chapter is organized as follows: first, a brief introduction into energy storage systems is presented, including a simple description of the workings of both batteries and supercapacitors. Next, a concise overview of the basic
design of a three-dimensional electrode is provided, along with the morphological considerations that are needed to ensure idealized electrochemical characteristics. Next, some basic principles of many of the experimental approaches used throughout this dissertation will be examined. In particular, the general principles of confocal microscopy used for microstructural investigation of bijels will be reviewed, along with a brief background on oscillatory rheology that is used to provide insights into the flow properties and mechanical stability of bijels and lastly the principles of the electrochemical measurements used to analyze the composite electrodes derived from bijels will be presented.

1.2. ENERGY STORAGE SYSTEMS

![Diagram of energy storage system](image)

**FIGURE 2. SIMPLE SCHEMATIC OF THE OVERAL DESIGN OF AN ENERGY STORAGE TECHNOLOGY.**

Batteries are one of the most widely used energy storage devices in our daily lives. In this digital age we currently live in, they are especially integral to our everyday operations. The simplest definition of a battery is a device that stores electricity through the form of chemical energy, and converts this chemical energy to electricity during use. Batteries consist of a positive electrode (cathode) and a negative electrode (anode)
separated by an ion conducting material, the electrolyte, as depicted in Figure 2. During a battery discharge cycle the electrochemical reaction occurring on the anode releases both electrons (which flow through the external circuit) and ions (which flow through the electrolyte to the other terminal, the cathode). The reaction that occurs simultaneously at the cathode accepts the electrons from the anode, completing the electrical circuit and generating an electric current. Secondary (rechargeable) batteries are able to take electrical energy from an outside source and reverse the reaction. Hence, these devices can be recharged and reused many times, but often at the price of a reduction in the amount of stored energy over time.

Electrochemical supercapacitors are a type of energy storage system that are used in applications that require high power, but do not need to simultaneously deliver high energy. Figure 3 is a simple schematic of the workings of an electrochemical supercapacitor. Just like batteries, the device is comprised of two electrodes (positive and negative) separated by an electrolyte. Positive charges accumulate at the positive electrode, and an equal number of negative charges accumulate in the electrolyte in the vicinity of the electrode’s surface, creating an electronic double-layer. The same (with opposite charges)
occurs at the negative electrode, creating an additional electronic double-layer. This allows for rapid charge and discharge of these devices. However, the total capacitance in these materials is relatively small due to the condition that charge storage only occurs at the surface of the material. In order to increase the amount of stored energy in supercapacitors, electrolytically active material that exhibits pseudocapacitive behavior, meaning that faradic charge transfer occurs through an electrochemical reduction-oxidation (redox) reaction, can be used. If the electrode is comprised of only pseudocapacitive material, it functions in the same manner as a rechargeable battery electrode as described above. Creating a device that contains an electrode with pseudocapacitive material and an electrode with a material that creates an electrochemical double-layer can greatly increase the amount of stored energy, while still maintaining fast charge and discharge rates. However, these devices still require drastic improvement in the areas of energy and power density in order to meet future energy demands.

1.3. THREE-DIMENSIONAL MICROSTRUCTURES FOR ENERGY STORAGE

Over the past decade, there have been great strides in the area of nanostructured electrodes, showing the ability to greatly increase the overall performance of the electrode through careful microstructural design\textsuperscript{16,25}. In order to understand how architectural development can aid in the performance of electrochemical systems, it is important to understand the basic design of an electrode. Composite electrodes are comprised of three major phases: a current collector, an electrolytically active phase, and the electrolyte that fills the pores. The current collector is the backbone of the electrode, and acts as a pathway for electrons to transport throughout the structure. Current collectors are made of electron
conducting materials such as carbon, nickel, copper and aluminum\textsuperscript{26}. The electrolytically active material depends on whether the electrode behaves as an anode or cathode and the particular energy storage technology; nonetheless, it is sandwiched between the ion conducting material (electrolyte) and the current collector.

![Diagram of electrode structures](image)

**Figure 4. Schematic of the structure of a composite electrode.** A) Typical 2D battery electrode design that is comprised of a thick active material layer. B) Thin film 2D battery electrode design comprised of a thin layer of active material on a 2D current collector. C) 3D electrode with a thin layer of active material.

To illustrate this, Figure 4 shows a variety of different electrode structures, including both 2D (Figure 4a & b) and 3D (Figure 4c, if extending the 2D representation to 3D) designs. Each schematic represents the same volume, displaying how the different designs can accommodate different amounts of active material within the same volume. Figure 4a presents a typical 2D battery electrode, with a thick active material layer. Since it has a large volume of active material, it can store a fairly large amount of energy. However, this comes as a sacrifice to how fast the material can be charged and discharged and still access the entirety of the active material. This can be better understood through considering the relationship between charge/discharge time and the thickness of the active layer\textsuperscript{25,27}:

$$t \sim \frac{l^2}{D}.$$
The diffusion time of ions in the active material \((t)\) is related to the square of the active material thickness \((L)\) over the diffusivity of the active material \((D)\). Thus, as the layer of the electrolytically active material increases, so does the diffusion time of ions within that layer, causing a reduction in the overall power density. Consequently, even though electrodes with the design of Figure 4a exhibit large energy densities due to the thick layer of active material, they will also have relatively low power densities. To increase the power density, one can design an electrode similar to that of Figure 4b, with a very thin layer of active material. However, as can be seen in the schematic, this allows for only a small volume of active material. Thus, the increase in power density comes at a cost of decreased volumetric energy density.

As described earlier, for an electrode to offer simultaneously large volumetric energy and power densities, an electrode with a design similar to Figure 4c is required. This design offers a thin layer of active material, facilitating large power densities, but also offers increased surface area for a large volume of active material within the given volume, enabling large energy densities. The actual manner in which the active material is organized throughout the 3D space can differ greatly from the schematic in Figure 4c, however a high surface area along with a thin layer of active material is required for the ideal electrode structure. In particular, materials with a bicontinuous microstructure inherently satisfy the first criteria for an idealized 3D electrode: a highly porous and connected pathway throughout a three-dimensional space\(^{28}\). Additionally, the dimensions of the pores should be in the micro to nanoscale range, enabling short transport paths for ions and electrons\(^{19}\). Through creating architectures that satisfy these criteria, electrodes can be designed to simultaneously offer large energy and power densities.
1.4. EXPERIMENTAL TECHNIQUES

1.4.1. CONFOCAL MICROSCOPY

Confocal microscopy is an imaging technique that is used throughout this dissertation for microstructural analysis of the soft materials of interest. The basic concept of confocal microscopy was patented by Marvin Minsky in 1957\textsuperscript{29} in order to overcome the challenges of traditional fluorescence microscopy, in which light from out of focus objects causes significant contrast issues with the plane of interest. Thus, only the outermost surface of an object was able to be clearly resolved, not allowing for sharp imaging of a 3D specimen. Minsky proposed to fix this issue through the use of a pinhole aperture that limits the field of illumination, rejecting any light scattering effects from areas other than the illuminated point of interest. This concept is illustrated in Figure 5. First, light from a laser (shown in blue) passes through a pinhole aperture to the fluorescent sample being imaged. This excites the fluorescent sample, and the reflected in focus (purple) and out-of-focus light is detected.
focus (grey dashed-line) light passes through an additional pinhole aperture that rejects the out-of-focus light. The word confocal stems from that fact the pinhole is conjugate to the focal plane. By varying the focal plane (through the objective position) one can reconstruct a 3D sample through individual 2D slices. Moreover, the thickness of these slices can be varied by the size of the aperture; the narrower the aperture, the thinner the obtained slices are, but at the cost of a reduced image intensity. Confocal images throughout this dissertation were acquired with a Vt-eye confocal scanner (Visitech International) attached to an inverted microscope (Axio Observer A1). The light source is a monochromatic laser ($\lambda = 491$ nm, Calypso, Cobolt AB) with an acousto-optic tunable filter (AOTF) to modulate the intensity of the laser. Additionally, a fast scanning confocal microscope was utilized for this work. This type of confocal microscope uses an acousto-optical deflector (AOD) crystal to scan in the horizontal direction along with a traditional galvanometer that scans in the vertical direction. This allows for image capture of 512 x 512 pixels images up to 129 frames per second. Typically, a frame rate of 29 fps was used with three different objectives: 100x, 20x and 4x producing images that span 66 $\mu$m, 312 $\mu$m and 1136 $\mu$m in each direction.

1.4.2. OSCILLATORY RHEOLOGY

Rheology is the study of the flow and deformation of materials, and has been used to better understand the flow behavior of a variety of materials such as colloidal gels\textsuperscript{30,31}, polymers\textsuperscript{32,33}, coatings\textsuperscript{34} and biological systems\textsuperscript{35}. In particular, oscillatory rheology is used throughout this dissertation to better understand the mechanical stability of bijels. In this type of rheology, a strain deformation is applied to the sample and the stress response
is measured. Broadly, a materials’ behavior can be classified into three categories: elastic, viscous, and viscoelastic. Elastic materials behave like solids and follow Hooke’s Law: when a stress is applied to the material, the resulting strain is completely recovered when that stress is removed. Viscous materials, like syrups and oils, behave like liquids in which there is a linear relationship between the applied shear stress and the shear rate. The soft materials studied throughout this dissertation fall under the category of viscoelastic materials, which exhibit a much more complex flow behavior and can behave both like a solid and a liquid depending upon the applied stress. The important measureable quantities obtained from rheological experiments for the purpose of this study are the storage (or elastic) modulus, $G'$, and the loss modulus, $G''$. The storage modulus is the ability of the material to store energy, and is a measure of the elasticity of a material. The loss modulus is the ability of the material to dissipate energy like a liquid. Thus, combined these quantities determine if the material is behaving more as a liquid or a solid. When $G'' > G'$, the material exhibits more of a liquid like behavior, conversely, when $G' > G''$ the material behaves more like a solid.

The two main tests used throughout this dissertation are aging tests and strain sweeps. For an aging test, both a constant strain ($\gamma = 0.01\%$) and constant frequency ($f = 1$ Hz) were applied to the sample and the storage and loss moduli were recorded over a set amount of time. This allows for monitoring of $G'$ and $G''$ over time. In oscillatory strain sweeps, the frequency ($f = 1$ Hz) is kept constant while the strain is varied over a wide range ($0.005\% < \gamma < 100\%$), and the storage and loss moduli are monitored throughout this test. In viscoelastic materials, when a large enough strain is applied to the sample, the
material will eventually break, causing a transformation in the material's behavior; a transition from solid like behavior to liquid like behavior will occur. The storage modulus will start to decrease, and there will be a point at which there is a crossover between the storage and loss moduli, that is when $G' = G''$. This point it called the yield stress, and is the necessary stress to provoke such a change in the material. This test also provides you with the linear viscoelastic region (LVR) of your material. This is the region of the material in which the storage modulus is independent of strain, i.e. you have a constant value for $G'$. The zero shear elastic modulus, $G'_0$, is calculated from this region. Figure 6 shows a schematic of a typical strain sweep test for viscoelastic materials.

**FIGURE 6. SCHEMATIC OF A TYPICAL OSCILLATORY STRAIN SWEEP FOR VISCOELASTIC MATERIALS. THE LVR IS CLEARLY SHOWN.**
1.4.3. ELECTROCHEMICAL MEASUREMENTS

In order to determine the electrochemical performance of our electrodes, including energy and power densities, a variety of electrochemical tests were performed on each electrode. These tests were performed using a Solartron CellTest System Model 1470E interfaced with CorrWare software that can be controlled using a computer.

![Cyclic Voltammetry Measurements](image)

**FIGURE 7. SCHEMATIC OF CYCLIC VOLTAMMETRY MEASUREMENTS, WHERE A) DISPLAYS THE POTENTIAL VERSUS TIME AND B) DISPLAYS THE CURRENT VERSUS TIME.**

The first tests performed on each sample are cyclic voltammetry (CV) tests. A representative example of this test is shown in Figure 7. As seen in Figure 7a, the voltage is linearly scanned between two different voltage limits ($V_1$ and $V_2$) at a specific scan rate ($\text{mV/s}$). Additionally, the current is monitored throughout this process, and plotting this versus voltage creates a CV curve, as shown in Figure 7b. These tests are performed in a three-electrode setup, with a working electrode (our sample), a reference electrode ($\text{Ag}/\text{AgCl}$) and a counter electrode (platinum wire). The reference electrode preserves the constant potential between the working electrode and itself, and the potential is measured between these two electrodes. The current, however, is measured between the counter...
electrode and the working electrode. The main role of the counter electrode is to ensure that current does not flow through the reference electrode, since if this occurred the potential of the reference electrode would be altered. A wide variety of information can be obtained from this experiment. For this dissertation, specific capacitances at varying scan rates were calculated. The specific capacitances of the electrodes can be calculated from the CV curves by using Equation 1:

$$Specific\ Capacitance\ (C_s) = \frac{\int_{V_1}^{V_2} i(V) dV}{\Delta V \cdot \mu m}$$

**EQUATION 1. SPECIFIC CAPACITANCE VALUES DERIVED FROM CV TESTS.**

where $\Delta V$ (V) is the applied potential window, $\mu$ (mV/s) is the scan rate, and $m$ (g) is the mass of the active material. Once these values are calculated, the energy and power densities can be determined. Energy densities can be calculated from the CV curves using Equation 2:

$$d_e = \frac{1}{2} C_s (\Delta V)^2$$

**EQUATION 2. ENERGY DENSITY FROM SPECIFIC CAPACITANCE VALUES.**

where $C_s$ (F/g) is the calculated specific capacitance and $\Delta V$ (V) is the potential window. Consequently, power densities were calculated using Equation 3:

$$d_p = \frac{d_e}{\Delta t}$$

**EQUATION 3. POWER DENSITY FROM SPECIFIC CAPACITANCE VALUES.**

where $d_e$ is the calculated energy density (Wh/kg) and $\Delta t$ is the time for a sweep segment.

To convert these values from gravimetric to volumetric densities, the mass of the active material in Equation 1 is replaced with the total volume of the electrode, creating
capacitance values with units of F/L. The energy and power densities are then recalculated using these values and Equation 2 and Equation 3.

The second type of electrochemical test utilized throughout this dissertation is a charge/discharge test. The same exact setup is used for this test that is used for the CV tests, including a working, reference and counter electrode immersed in an electrolyte. For this test, a constant current is applied to the sample until a certain voltage is reached, and the voltage response is measured. Charge/discharge curves are then constructed by plotting the voltage versus time. Similarly to CV tests, the specific capacitance of the electrode can also be calculated from the galvanostatic discharge curves using Equation 4:

\[
Specific\ :Capacitance(C_{s}) = \frac{I\Delta t}{m\Delta V}
\]

EQUATION 4. SPECIFIC CAPACITANCE VALUES DERIVED FROM CHARGE/DISCHARGE CURVES.

where \( I \) (A) is the discharge current, \( \Delta t \) is the time for a full discharge, \( m \) (g) is the mass of the active material, and \( \Delta V \) (V) is the potential window. Additionally, the power and energy densities can then be calculated using these values and Equation 2 and Equation 3. To convert these values from gravimetric to volumetric densities, the mass of the active material in Equation 4 is replaced with the total volume of the electrode. The energy and power densities are then recalculated using these values and Equation 2 and Equation 3.

1.5. STRUCTURE OF THE DISSERTATION

The rest of the dissertation is structured as follows. In Chapter 2, I introduce a relatively new class of soft materials, bijels, and describe how their rheology provides insights into their ability to be post processed into an array of materials. Chapter 3
describes a new class of bijels, termed bridged bijels, and shows how the internal microstructure of this soft material allows for the ability to access exceedingly large domains, not accessible in a simple bijel. Additionally, the rheological behavior of bijels and bridged bijels was explored further, analyzing the relationship between the zero shear elastic modulus and the particle volume fraction. Combined, these two chapters provide key insights into the mechanical stability of bijels, which provides important insights for the ability to process these soft materials into a myriad of materials. Chapter 4 explores composite electrodes derived from bijels, showing two different chemistries as examples: nickel/nickel hydroxide composite electrodes, and a carbon silicon anode for lithium ion batteries. Additionally, I show that the unique morphological control afforded by our processing technique leads to superior electrochemical performance for these composites.
2. MAKING A ROBUST INTERFACIAL SCAFFOLD: BIJEL RHEOLOGY AND ITS LINK TO PROCESSABILITY

2.1. BACKGROUND

2.1.1. PARTICLES AT FLUID INTERFACES

The natural phenomena of particles stabilizing fluid interfaces was first observed by Ramsden\textsuperscript{36} in the early 20\textsuperscript{th} century. Since the discovery of Pickering Emulsions\textsuperscript{37}, in which solid particles stabilize a dispersed phase of droplets, the idea of particles at fluid interfaces has been studied in great detail as well as heavily implemented into our everyday lives. This phenomenon is key in industries such as cosmetics, personal care products, oil and food\textsuperscript{38-41}, and more recently has been shown to be promising in areas such as drug delivery, catalysis, and composite materials\textsuperscript{42-44}. Even though this phenomenon is widely used in industry today, it is still being extensively researched in order to better understand the stabilization mechanism and how it relates to key characteristics of the systems, such as microstructure, rheology and stability.

Solid particles can be kinetically trapped at a fluid-fluid interface by reducing the shared interfacial area of the fluids and therefore reducing the systems free energy. Through carefully choosing the wettability of the particles with the two fluids, the total energy cost involved can be reduced. The particle wettability is often quantified by the three-phase contact angle, $\theta$, defined as the angle between the tangent to the solid particle surface and the liquid-liquid interface and the fluid interface, as can be seen in Figure 8\textsuperscript{45}. The contact angle depends on the interfacial tensions ($\gamma$) between the particle (p), oil (o), and water (w) interfaces according to Young’s Equation\textsuperscript{46}:
\[ \cos \theta = \frac{\gamma_{po} - \gamma_{pw}}{\gamma_{ow}} \]

**Equation 5. Young’s Equation Defining the Three-Phase Contact Angle of a Particle at the Interface of Two Fluids.**

![Diagram of three-phase contact angle](image)

**Figure 8. The Three-Phase Contact Angle, \( \theta \).**

This three-phase contact angle is measured through the more polar (aqueous) phase, by convention. Hydrophilic particles are preferentially wet by the water phase \((\gamma_{pw} > \gamma_{po})\) with \(0^\circ \leq \theta < 90^\circ\), while hydrophobic particles are preferentially wet by the oil phase \((\gamma_{po} > \gamma_{pw})\), with \(90^\circ < \theta \leq 180^\circ\). If the particle is wet by both the water and oil phase equally, then \(\gamma_{po} = \gamma_{pw}\), and the right hand side of Young’s Equation 5 becomes 0, such that \(\theta = 90^\circ\). These particles are termed “neutrally-wetting.” Additionally, the presence of the particle can actually deform the fluid interface, such that when multiple particles are adsorbed to the interface, the deformation of the fluid interface can lengthen to distances similar to the capillary length, \(\lambda\), defined as:

\[ \lambda = \frac{1}{\sqrt{\rho_w - \rho_o)g/\gamma_{ow}}} \]

where \(\rho\) is the density of the phases and \(g\) is the gravitational force. Thus, when multiple particles lay at the interface and their menisci overlap, attractive, long-range capillary forces between the particles could direct particles closer to one another. This will be
important in later discussions on the processability of the bijels. The desorption energy of a single particle at a fluid-fluid interface, provided that the gravitational effects can be neglected due to small particle size, is given by\(^{45}\):

\[
\Delta G = \pi r_p^2 \gamma_{ow} (1 - |\cos \theta|)^2,
\]

_EQUATION 6. THE DETACHMENT ENERGY OF A PARTICLE AT A FLUID-FLUID INTERFACE._

where \(\Delta G\) is the energy required to detach a particle from the fluid-fluid interface, \(r_p\) is the particle radius, \(\gamma_{ow}\) is the interfacial tension, and \(\theta\) is the three-phase contact angle. In a water, 2-6 lutidine system with neutrally-wetting (\(\theta = 90^\circ\)) spherical particles of \(r_p = 700\) nm, and \(\gamma_{ow} = 0.8 \) mN m\(^{-1}\) at 60°C, this energy is on the order of magnitude of \(10^6 kT\), where \(k\) is the Boltzmann constant and \(T\) is the absolute temperature\(^{47}\). This energy is several orders of magnitude greater than that of their thermal energy, thus once particles are adsorbed to the interface, they will be irreversibly trapped. When dealing with a single fluid-fluid system and set particle size, the contact angle, \(\theta\), is the only parameter that dictates the stability of the particles at the fluid-fluid interface. The ability to tune the wetting properties of the colloids to neutrally-wetting conditions is key when creating bijels, as will be discussed in later sections.

2.1.2. Bicontinuous Interfacially Jammed Emulsion Gels

As described in Section 2.1.1, since the discovery of Pickering Emulsions, the phenomena of particles stabilizing fluid interfaces has been of great technological interest. Traditionally, these Pickering Emulsions are formed through agitation of a sample containing particles and two or more immiscible fluids. However, such structures can also form via temperature induced phase separation of two partially miscible fluids. In
particular, some binary fluid systems can phase separate via two different kinetic pathways: nucleation and growth (producing droplets) and spinodal decomposition. This second pathway, spinodal decomposition, creates two, bicontinuous interpenetrating fluid domains. In 2005, it was proposed through lattice-Boltzmann simulations that the same idea of stabilizing spherical or aspherical emulsion droplets can be used to stabilize fluids undergoing spinodal decomposition\textsuperscript{48}. These new soft materials were termed bicontinuous interfacially jammed emulsion gels (bijels), and the result of these simulations is shown in Figure 9. The authors realized that there has been a recent surge in the area of nanoscale and mesoscale materials, and that materials formed out of non-equilibrium processes could offer more control at the pertinent length scales. Non-equilibrium processes not only rely on thermodynamic conditions, but also the process history\textsuperscript{49} and such materials can become trapped in a metastable state and thus can be more robust to changes in thermodynamic conditions than an equilibrium phase material.

![Figure 9: Lattice-Boltzmann simulations predict that particles can arrest binary fluids undergoing spinodal decomposition through particle jamming (reproduced from Ref. 48).](image)

In order to better understand the formation of bijels, let's first consider the phase separation processes that occur in a binary fluid system containing two partially miscible
fluids. Consider a phase diagram like Figure 10, which is a schematic of the binary fluid system of water and 2,6-lutidine (W/L). This binary fluid system exhibits a miscibility gap, where there are certain temperatures and compositions in which the two fluids are miscible. However, when certain compositions and temperatures are reached, it will phase separate via two different kinetic pathways: nucleation and growth and spinodal decomposition. Nucleation and growth creates droplets of a dispersed phase in a continuous phase. Spinodal decomposition, on the other hand, produces two self-similar, interpenetrating fluid domains. In order to access spinodal decomposition, the composition of the fluids must be tuned to the critical composition ($x_C$) and the temperature must be increased to a temperature above that of the lower critical solution temperature (LCST, $T_C$).

![Figure 10. Schematic depicting the spinodal phase diagram of water/2,6-lutidine. The critical temperature ($T_C$) and critical composition ($x_C$) are clearly displayed on the graph.](image)

As seen in Figure 10, there are two different curves displayed and the outer most curve represents the binodal curve. This curve signifies a thermodynamic limit as to when
the fluids are miscible, and when they will phase separate, and is given by \( \partial \Delta G^{\text{mix}} / \partial x_a < 0 \).

Phase separation can occur through of a variety of different external stimulants, this dissertation considers fluids that undergo phase separation through a change in temperature. The second curve defines the spinodal region (depicted in Figure 10 by the innermost curve), and is given by \( \partial^2 \Delta G^{\text{mix}} / \partial x_a^2 < 0 \), and intersects the binodal curve at the critical composition and temperature. This curve represents the unstable regime, where the initial mixture can no longer endure small changes in composition and remain stable. The onset of spinodal decomposition causes separation of the fluids spontaneously throughout the entire sample; there is no energy barrier for the system to overcome. The resulting morphology for this type of phase separation, as mentioned previously, is two, bicontinuous fluid domains that span the entire structure. Over time, the fluid domains will coarsen due to the overall desire to reduce the total energy of the system. This can occur by reducing the total area in which the two fluids are in contact, thus reducing the surface free energy, and creating larger domains. If the system is unperturbed, phase separation will continue until the phases have completely demixed, creating a minimum area of contact between the two phases. However, just like how particles can stabilize droplets before they completely coalesce, colloids can be introduced into the sample before phase separation occurs and arrest the sample at varying length scales for the self-similar domains.
Figure 11. Schematic depicting the formation of bijels. A) The colloids are dispersed in the binary fluid mixture at a temperature in which the fluids are still miscible. B) When the temperature is increased past the lower critical solution temperature, the fluids start to separate and the particles adsorb to the fluid-fluid interface. C) The particles become jammed and create the final structure.

Bijel formation follows the steps depicted in Figure 11. First, neutrally-wetting colloidal particles are dispersed in the single fluid phase (Figure 11a). It is important that these particles have a contact angle close to 90°, such that the particles do not preferentially wet either phase allowing them to adsorb to the fluid interface once it is formed. Additionally, these particles can freely diffuse throughout the sample via Brownian motion. When the sample is quenched into the unstable region, the particles will go to the fluid interface (Figure 11b) in order to reduce the interfacial contact area of the two fluids. At this early stage, the interface of the fluids is much larger than that of the particles adsorbed to the interface, and the domains will continue to coarsen in order to reduce the total energy of the system. It has also been predicted that this step will help in reducing the necks that can form between adjacent fluid channels. The fluid domains will coarsen until the interfacially area is sufficiently reduced to just accommodate the particles (Figure 11c). Further coarsening can only occur if the particles become detached from the interface, and as mentioned in Section 2.1.1, the desorption energy of a neutrally wetting particle is several orders of magnitude larger than its thermal energy. Thus, it is thermodynamically
favorable for the particles to remain at the interface, and hence arrest the spinodal structure in a metastable state. Additionally, the fluid domains are separated by a cohesive monolayer of particles that span the entire sample, creating a gel. Thus, bijels have properties of both emulsions and gels (therefore the name bicontinuous interfacially jammed emulsion gels).

![Figure 12. Time series showing the formation of a bijel with $\phi = 2\%$. The time difference between samples is 0.7 s (reproduced from Ref. 51).](image)

Bijels were realized experimentally in 2007, a mere two years after simulations suggested that particles can arrest fluids undergoing spinodal decomposition$^{51}$. The binary
fluid system chosen was that of water and 2,6-lutidine (Figure 10) with colloidal silica particles that were carefully tuned to be neutrally wetting to the two phases. Here, bijels were creating by dispersing silica in the single phase, and quickly quenching the sample into the spinodal regime. A timed series showing the formation of bijels is shown in Figure 12\textsuperscript{51}. Here, the authors used a particle volume fraction (ϕ) of 2\%, and each sequential image is 0.7 s after the last image. Additionally, unlike prior attempts to create sample spanning bijel samples\textsuperscript{52,53}, the authors were able to create samples up to 1 mm thick, producing samples that spanned several domains. However, in order to create such structures, it was determined that a fast quench (17°C/min) was necessary to construct samples with finite thicknesses\textsuperscript{51}. Additionally, the authors showed that the size of the fluid domains (ξ) can be tuned solely by the particle volume fraction. If you consider spheres in a closed-packed manner, with monolayer coverage on a spherical domain, you can arrive at an equation for the domains which depends on both the diameter of the particles (d) as well as the particle volume fraction: 

\[ \xi = \frac{\pi}{\sqrt{3}}(d/\phi) \] 

Thus, the size of the fluid domains is inversely proportional to \( \phi \). It was determined that this relationship does not hold up at small values of \( \phi \); the linear relations starts to fall off when \( \phi \leq 1 \% \), with is believed to be due to gravitational effects\textsuperscript{51}. This will become important in Chapter 3, where I introduce a manner in which to access exceedingly large domains.\textsuperscript{55}. Additionally, when bijels were first introduced, it was believed that they were robust enough to act as a flow reactor, essentially allowing for fluid flow in each fluid domain. While it was shown that for the W/L system, the silica network remains intact after fluid remixing, this is not a universal result.
for bijels and is important later on in this chapter when considering these materials as a templates to create an array of materials\textsuperscript{56}.

Using the W/L system, it has been shown that bijels can be chemically converted a myriad of bicontinuous and hierarchical porous materials, including polymers, metals, ceramics, and composites\textsuperscript{57-59}. In order to process these soft materials, the incompatibility of the two fluids is exploited to polymerize one fluid domain and transform the soft material into a bicontinuous polymer scaffold. In particular, it has been shown that monomers that have a preference for one fluid phase over the other will selectively partition into one fluid phase. Through gravitational forces and diffusion, the monomer and fluid phase will eventually equilibrate, and the monomer can be crosslinked via exposure to UV light. Using bijels as soft mater templates in this way allows for a wide variety of processing possibilities. First, an extensive range of UV curable monomers can be used to create the polymer scaffold. The only requirement is that the monomer must selectively prefer either water or 2,6-lutidine. Additionally, the unique nature of bijels allows for tuning the domains over a wide range simply by changing the particle diameter or volume fraction\textsuperscript{51}. Furthermore, the cross-linking density of the polymer can be varied through the amount of monomer added to the bijel sample. Combined, these two processing techniques have been used to create hierarchically porous silver monoliths, with the ability to easily tune both the macro and micro pores\textsuperscript{59}. Additionally, through varying the crosslinking density and creating a very dense polymer, one can coat the polymer domains and create “shell” type materials\textsuperscript{57}. This will be explored in more detail in Chapter 4, as a nickel shell is created and used as the backbone for a composite electrode.
However, as this chapter aims to show, the robustness of the W/L system is not universal to all bijel systems. In particular, the jamming of particles at the fluid interface for W/L has been shown to create a “monogel,” even upon remixing of the two fluids the layer of silica stays intact\textsuperscript{56}. This monogel formation, and the ability of the sample to be able to withstand large gradients in chemical composition is key to the ability of these materials to be post processed. The rest of this chapter outlines the various bijel systems that have been experimentally reported in research, and introduces two other binary fluids systems that could potentially be used to expand upon the existing monomer set used to create polymer scaffolds. Next, a series of rheological and confocal microscopy experiments will be presented to better understand the ability of bijels to be processed into an array of materials. In particular, this study aims to show that without formation of a monogel, the bijel is highly sensitive to gradients in chemical composition, which can lead to mechanical failure during processing.
2.1.3. WATER/2,6-LUTIDINE SYSTEM

![Spinodal phase diagram for the 2,6-lutidine and water system](image)

FIGURE 13. SPINODAL PHASE DIAGRAM FOR THE 2,6-LUTIDINE AND WATER SYSTEM ((REPRODUCED FROM REF. 48)).

A binary fluid mixture of water and 2,6-lutidine has a spinodal phase diagram as shown in Figure 13\(^47\). This system has a LCST of 34.1°C and a critical composition of \(x_{lut} = 0.0064\). As mentioned previously, the first successful bijel was obtained with this fluid system along with colloidal silica to stabilize the structure. The silica must be neutrally-wetting to both phases in order to ensure bijel formation, and synthesizing silica that fits these characteristics is not trivial. The interactions of silica with water and lutidine and how this effects bijel formation has been studied elsewhere\(^56,60,61\), but it important to note that the ability to carefully tune the wettability of the particles is crucial for bijel formation. The specific set of conditions to synthesize W/L silica particles is outlined in Section 2.2.1. Figure 14 displays the typical microstructure of bijels formed in this system, showing both large domain (low particle volume fraction) and small domain (high particle volume fraction) bijels.
2.1.4. Nitromethane/Ethylene Glycol System

![Phase Diagram for the NM/EG System](image)

**FIGURE 14.** Confocal image of a W/L bijel with $\phi = 0.01$ and 0.04.

**FIGURE 15.** Phase diagram for the NM/EG system (reproduced from Ref. 63).
Recently a new bijel system was introduced that uses a binary fluid system containing nitromethane and ethylene glycol (NM/EG). It was proposed that this system could offer many advantages over the W/L system due to it exhibiting an upper critical solution temperature (UCST) instead of a LCST, the stability of the bijel at room temperature, and a phase diagram that exhibits a higher degree of symmetry\(^6\). This system has a critical mole fraction of \(x_{NM} = 0.64\) and an UCST of 40°C, as can be seen in the phase diagram (Figure 15)\(^6\). The authors used silica particles that had been treated with a silanization agent to render the particles neutrally-wetting. Additionally, the authors were able to stabilize structures using particles that were sub-100nm, creating fluid domains under 10 microns. Thus, due to these advantages, it was desirous to process these materials in the same manner as the W/L system. However, as the remainder of the this chapter aims to show through rheological and confocal microscopy experiments, processing this system is not as straight forward as the W/L system. A typical confocal microscopy image of a NM/EG bijel is shown in Figure 16.
2.1.5. OTHER BINARY LIQUID SYSTEMS

As mentioned previously, in literature there are currently only two binary fluid systems have been experimentally utilized to form bijels. However, there are a myriad of fluid systems that undergo spinodal decomposition that can be used to form this new soft material. In particular, when looking for new potential systems, it is desirous to find binary fluid systems that exhibit either an UCST or LCST within a reasonable temperature range that can easily be used in lab (10°C < T < 80°C) and also has a nearly symmetric volume fraction of phases at the critical composition. As such, other fluid systems have been explored in order to expand upon the current set of fluids that can be used to synthesize bijels. Currently, two additional systems have been discovered that can render bijels.
2.1.5.1. *Isobutyric Acid and Water*

![Phase Diagram](image)

**FIGURE 17. PHASE DIAGRAM FOR THE WATER AND ISOBUTYRIC ACID SYSTEM (REPRODUCED FROM REF. 64).**

A system consisting of isobutyric acid and water (I/W) exhibits the phase behavior shown in Figure 17, with an UCST of 26.1°C and a critical composition of 38.8 wt% isobutyric acid\(^6\). Silica particles for this system were synthesized in the same manner as that of W/L bijels, with a reduced drying time, rendering them partially more hydrophilic than W/L particles. This system can provide a unique processing technique, given the drastic differences in freezing temperatures between water (0°C) and isobutyric acid (-47°C). As explained above, processing of the W/L or NM/EG system requires that the monomer selectively partitions into one of the fluid phases. However, for this system, instead of exploiting the incompatible chemistries of the fluid phases, we can exploit the differences in melting points. This will allow us to expand upon our current set of the monomers that can be used with the W/L and NM/EG system, creating an even more robust platform to create bicontinuous polymer scaffolds. To briefly show this, two polymers that could not be used in the W/L system were used to create polymer scaffolds.
derived from bijels: Poly(N-isopropylacrylamide) and acrylamide. In particular, poly(N-isopropylacrylamide) is a stimuli responsive polymer that has many applications in the biomedical sector, leading to potential uses as cell scaffolds or other smart devices. A confocal image of a bijel synthesized using the I/W system is shown in Figure 18.
2.1.5.2. *Succinonitrile and Water*

![Phase Diagram of the Water and Succinonitrile System](image)

**Figure 19.** Phase diagram of the water and succinonitrile system (reproduced from Ref. 65).

The spinodal curve for the succinonitrile and water system (S/W) is shown in Figure 19. This system has a critical composition of $x_{\text{water}} = 0.827$ and an UCST of 57°C.

Furthermore, it has similar characteristics to that of the NM/EG system, in that it also exhibits an UCST, and allows for processing at room temperature. Additionally, this system is unique in that the succinonitrile phase is actually solid at room temperature. Thus, this system can be processed in a similar manner to that of the I/W system. Since succinonitrile is solid at room temperature, the water phase can be drained and replaced with any monomer. While this system has not yet been post-processed, the use of this system offers great potential as a robust platform to transform bijels into any polymer that is UV curable. Figure 20 shows a confocal microscopy image of a bijel created through this system. Silica particles for this system are synthesized in the same manner as the NM/EG system, with
the surface chemistry of the colloids tuned to be neutrally wetting to both water and succinonitrile.

![Figure 20. Confocal microscopy image of BIJEL in the S/W system.](image)

2.2. EXPERIMENTAL METHODS

2.2.1. PARTICLE SYNTHESIS AND FUNCTIONALIZATION

The colloids used throughout this dissertation are fluorescent spherical silica particles, due to the ability to easily modify their surface chemistry, size and monodispersity control, and low cost. However, in principle a wide variety of colloids such as metal oxides (titania, zirconia, or alumina), polymers (poly(methyl methacrylate) or polystyrene) or metals (carbon, nickel or gold) could be employed as long as their wettability can be controlled to the same degree as silica. Additionally, other particle shapes such as rods and cubes can be explored. In particular, it recently has been shown that rod shaped particles can be used to stabilize the NM/EG system\textsuperscript{66}. It has also been shown that graphene oxide sheets can stabilize the W/L system, however the resulting
microstructure is quite different than the regular bijel structure due to the rigidity of the graphene oxide sheets. Combined, these two studies show how a variety of different materials and particle shapes can be used to stabilize two fluids undergoing spinodal decomposition, as long as the surface chemistry can be carefully tuned to be neutrally-wetting.

![Figure 21. SEM Picture of HMDS Modified Stöber Silica](image)

The silica synthesis procedure used to create fluorescent, monodisperse silica follows the method developed by Stöber in 1968 and that was later modified by both Bogush and Van Blaaderen to incorporate fluorescent dye. Fluorescent particles are needed to properly image using a confocal microscope. Two types of fluorescent Stöber silica colloids with an average diameter of \( \langle d \rangle = 410 \text{ nm} \) and a coefficient of variation \( CV = 3.2\% \) were used in this study, as shown in Figure 21. Silica synthesis begins with combining 12.5 mg of rhodamine B isothiocyanate dye (RITC, Sigma Aldrich) with 50 mg of 3-aminopropyltriethoxysilane (APS, ≥98%, Sigma Aldrich) in 10 mL of anhydrous ethanol and stirred overnight for at least 12 hours to create the conjugated dye mixture. In order to prevent unwanted photobleaching of the dye, the vial is covered with aluminum foil. As
shown in Figure 22, this creates a dye compound that can be easily incorporated into the silica during synthesis.

![Diagram of dye molecules](image)

**FIGURE 22. REACTION OF THE APS AND RITC DYE TO FORM A CONJUGATED DYE MIXTURE.**

Particles were then synthesized by combining 35 mL of anhydrous ethanol, 10 mL ammonia solution (35% w/w, Fisher) and 5 mL of the conjugated dye solution in a flask, followed by the addition of 4.18 mL of tetraethylorthosilicate (TEOS, ≥99%, Sigma-Aldrich), subsequently stirring for at least 12 hours\(^{69,70}\). These monodisperse silica particles are synthesized according to the following reaction:

\[
\text{Si(OC}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH}.
\]

The ratios of the reagents determine the size of the particles, thus particles with varying sizes can be synthesized through this route. The dye molecules attach to the functional groups of the silica spheres as the colloids grow in solution, creating fluorescent particles. A schematic of the surface chemistry of these particles is shown in Figure 23. As explained previously, obtaining a three-phase contact angle close to 90° is crucial for bijel formation. Recently, it has been shown that nanosized particles (80 nm) have a wider window for
their contact angle that allows for the formation of sample-spanning bijels\textsuperscript{71}. Nonetheless, the colloids used throughout this dissertation fall between the range of 400 nm – 700 nm, thus synthesizing particles with contact angles close to $90^\circ$ is crucial to create sample spanning bijels. During dye synthesis, APS is used in excess, and it is believed that it renders the particles more hydrophilic through the addition of amine groups to the surface of the particles\textsuperscript{60}. Additionally, the drying process provides a further route to render the particles neutrally-wetting\textsuperscript{60}. The particles were washed by repeated centrifugation in deionized water and carefully dried at 70 °C to achieve near-neutral wetting properties\textsuperscript{60,61}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure23.png}
\caption{Schematic of the surface chemistry for the RITC-dyed silica particles.}
\end{figure}

For NM/EG bijels, the surface chemistry of the particles was rendered partially hydrophobic by adding 3.5 mL of hexamethyldisilazane (HMDS, 98%, Alfa Aesar) directly to the reaction flask 3 hours after the addition of TEOS. Here, this silanization process attaches methyl groups to the silica surface to render them more hydrophobic. The surface chemistry of these particles is shown in Figure 24. The particles were washed in ethanol and dried at 120 °C under vacuum. These particles are not as sensitive to the drying procedure as W/L particles, and thus tend to be more reproducible.
2.2.2. BIJEL FORMATION

W/L bijels were formed by dispersing the silica particles in ultrapure water using a sonic probe (Branson Sonifier 250). An appropriate amount of 2,6-lutidine was then added to give a near-critical composition (lutidine mole fraction $x_L \approx 0.064$), and 200, 400, or 600 μL of the single-phase suspension was transferred to cylindrical microscopy vials of 5, 7, or 15 mm inner diameter (i.d.), respectively. W/L bijels are formed upon warming (LCST $\approx 34 ^\circ C$), and these were prepared by ramping the samples into the unstable region in a microwave oven and quickly transferring them to an incubator maintained at 60$^\circ$C as described previously$^{57}$. NM/EG bijels form upon cooling (UCST $\approx 40 ^\circ C$), and were prepared by dispersing the HMDS-modified silica in the critical mixture ($x_{NM} \approx 0.633$) via sonication, which concurrently heated the mixture above the UCST. The suspension was then transferred into thin capillaries preheated to 50$^\circ$C (400 μm path length, Vitrocom) and rapidly quenched into the unstable region by placing the containers on a chilled aluminum block. Bulk NM/EG bijels for materials processing were prepared in pre-heated cylindrical
vials of 3 mm i.d. and quenched in an ethanol bath maintained at -10 °C.

**FIGURE 25. SCHEMATIC REPRESENTATION SHOWING THE SELECTIVE POLYMERIZATION OF A BIJEL.** (A) A 3-DIMENSIONAL BIJEL IS FORMED BY ARRESTED SPINODAL DECOMPOSITION OF PARTIALLY MISCELLABLE FLUIDS BY COLLOIDAL PARTICLES THAT JAM AT THE INTERFACE. (B) THE BIJEL SURFACE IS EXPOSED TO A RESERVOIR OF LIQUID MONOMER THAT PREFERENTIALLY PARTITIONS INTO ONE FLUID PHASE. (C) THE FLUID COMPOSITION OF ONE BIJEL PHASE IS MODIFIED WHILE PRESERVING THE MORPHOLOGY. (D) THE MONOMER IS CURED VIA UV PHOTOPOLYMERIZATION TO FORM A BICONTINUOUS MACROPOROUS SOLID AND THE REMAINING LIQUID IS DRAINED.

Bijels were transformed into bicontinuous macroporous solids by selective polymerization of liquid UV-curable monomers as shown schematically in Figure 25. For this study trimethylolpropane triacrylate (TMPTA) and poly(ethylene glycol) diacrylate (MW 600, PEGDA) that were kindly provided by Sartomer were used. The monomers were mixed with a photoinitiator (Darocur 1173, Ciba) and a reservoir was then placed on the top surface of a bijel to initiate the selective partitioning of the monomer solution into one fluid phase (Figure 25b). After complete solvent exchange (Figure 25c), the monomer-rich phase of the bijel was crosslinked using a UV lamp (Omnicure 1000), and the remaining liquid was drained (Figure 25d). Digital images of the final polymer scaffolds are shown in Figure 26.
2.2.3. RHEOMETRY

Rheological measurements were performed using a stress-controlled rheometer (MCR 301, Anton-Paar) with parallel-plate geometry and a gap height of 100 μm. Bijels were formed on the rheometer stage using an integrated Peltier heating/cooling system operating at the maximum available rates of about 25 and 10°C/min for heating and cooling, respectively. The rheometer was also equipped with a Peltier hood to promote a uniform temperature throughout the sample, and minimize solvent evaporation. For each sample, critical suspensions initially in the single-fluid phase were transferred onto the rheometer and pre-sheared at $\gamma = 800 \text{ s}^{-1}$ for 30 s. Samples were then quenched into the two-phase region while recording the storage and loss moduli ($G'$ and $G''$, respectively) every 1 s at a constant oscillatory strain of $\gamma = 0.1\%$ and frequency $f = 1 \text{ Hz}$ to monitor the gelation process. In some experiments the samples were allowed to age for a given duration and then heated or cooled back into the single-phase region. The measurements
were found to be reproducible and geometry independent, indicating that our results were not contaminated by wall slip, as shown in Figure 27.

**FIGURE 27. EVOLUTION OF THE STORAGE ($G'$ – CLOSED SYMBOLS) AND LOSS ($G''$ – OPEN SYMBOLS) MODULI IN THREE NM/EG BIJEL SAMPLES PREPARED AT $\phi_p = 3\%$ DEMONSTRATING THE REPRODUCIBILITY OF THE RHEOLOGICAL MEASUREMENTS.**

### 2.2.4. MICROSCOPY

Bijels were imaged using a confocal scanner (Vt-eye, Visitech International) attached to an inverted microscope (Axio Observer, Carl Zeiss Microimaging, Inc.) with a $20\times, NA = 0.4$ objective. To assess the effect of fluid remixing on the microstructure, W/L bijels aged for 20 min in an oven at 60°C were cooled to 20°C on the microscope stage by free convection while the microstructure was visualized over time. An analogous experiment was performed with NM/EG bijels, instead using a steel block at 55°C to warm specimens back into the single-phase region. Scanning electron microscopy (SEM) was performed on polymerized bijels using a Quanta 3D microscope (FEI Company). Prior to
imaging, the silica particles were carefully etched from the polymer surfaces using an HF solution (10% v/v) and the samples were dried thoroughly before depositing a thin layer of iridium onto their surfaces using a sputter coater (South Bay Technologies).

2.2.5. INTERFACIAL TENSION MEASUREMENTS

Interfacial Tension Measurements: Nitromethane (99+%, Acros Organics), ethylene glycol (99.8%, Sigma Aldrich) and toluene (Fisher Scientific) were used as received. The monomer TMPTA (Sartomer, SR351) or PEGDA (Sartomer, SR610) was mixed with photoinitiator 2-hydroxy-2-methylpropiophenone (Aldrich = Darocur 1173) at a mass ratio of 99:1. Such mixtures were pipetted into the NM-rich phase at volume ratios of ≈1:10. Interfacial tensions were measured using the pendant-drop method on a Krüss EasyDrop instrument (model FM40Mk2), equipped with a level environmental chamber (Thermostat TC3010), connected to a circulator (Julabo F12). The temperature near the sample, ranging from 15.8 to 33.8 °C, was monitored with a thermocouple (LakeShore 331). The chamber was sealed with parafilm and regularly flushed with dry nitrogen gas to avoid contamination with (condensed) water. A rectangular glass container had been filled with the less dense phase (EG-rich), while a glass syringe (needle diameter 1.82 mm, Starrett micrometer) contained the droplet phase (NM-rich). Droplets were delivered at a set flow rate of 100 μL/min to volumes of 9 to 28 μL using a computer-controlled dosing unit, and were allowed to equilibrate for ≈5 min before digital snapshots were recorded from the side. As the needle reservoir can be at a different temperature than the needle tip (which is in the environmental chamber), droplets had a tendency to shrink over time. Hence, results were regularly checked for their dependence on equilibration time (2.5 to 15 min) and
droplet volume. Interfacial-tension values were extracted by fitting the Young-Laplace equation to the recorded drop profiles. Results are very sensitive to the densities provided for the liquid mixtures. Therefore, the liquid densities were measured at the corresponding temperatures using a density meter (Anton Paar, DMA 4500). Interfacial-tension errors are estimated to be 0.035 mN/m at room temperature up to 0.058 mN/m at lower/higher temperatures.

2.3. INTRODUCTION

Given their novelty, elegance, complexity, unique and advantageous morphology, and the breadth of available outlets for their use, bijels show much promise as a new and emerging class of soft matter with a significant need for experimental studies that facilitate their proliferation in both research and industry. In this chapter, we present a new set of confocal microscopy and rheology experiments that identify the key characteristics of bijels that mediate their processability into functional materials.

As mentioned previously, a reliable and flexible protocol has been developed for template-based synthesis of a variety of materials and composites with bicontinuous spinodal-like microstructure. Exposing a bijel to a liquid reservoir with selective miscibility in, or strong preference for, one of the fluid phases can alter the chemical composition inside the corresponding fluid channels. This allows the selective polymerization of fluid domains in a bijel (Figure 25), which is the key step for the processing protocol mentioned above. Here, the external reservoir consists of a liquid monomer that can be chemically crosslinked with exposure to ultraviolet light in the presence of a radical photoinitiator. The process provides control over a number of
processing parameters given the abundance of hydrophobic/hydrophilic monomers that can be polymerized through free-radical reactions, the ability to control the polymer crosslink density, and wide control over the width of the fluid channels (macropores in the polymerized scaffold) through the particle volume fraction and size\textsuperscript{24,57}.

As mentioned previously, a new bijel system consisting of nitromethane and ethylene glycol (NM/EG) with an upper critical solution temperature (UCST) $\approx 40^\circ$C and nitromethane mole fraction $x_{\text{NM}} = 0.633$, stabilized by silica microspheres was reported with several potential advantages over the W/L system\textsuperscript{63}. These included a more forgiving and reproducible method for tuning the particle-liquid affinities, a phase diagram with a higher degree of symmetry\textsuperscript{62}, and mechanical stability of the bijel (immiscibility of the fluid constituents) at room temperature. However, we observed that this system presented challenges for materials processing even with selectively miscible monomers; introduction of a monomer into this system typically resulted in mechanical failure and collapse of the bijel backbone. By exploring the rheological properties of these two bijel systems (W/L and NM/EG) we found that the extent of particle attraction at the interface mediates the bijel’s ability to withstand changes in its chemical makeup without altering its morphology. Bijels stabilized by interfacial tension alone are more easily damaged or destroyed when subjected to steep gradients in chemical composition. This undesired breakdown could result from a spatially heterogeneous distribution of the interfacial tension and concomitant Marangoni stresses along the particle-laden interface\textsuperscript{72} leading to deformation and rupturing of the fluid domains. Conversely, bijels formed with sufficiently attractive particles at the interface (e.g., via van der Waals forces\textsuperscript{56}) can offer enhanced stability.
against structural rearrangements during solvent exchange and provide a robust template for the synthesis of bicontinuous macroporous polymer scaffolds. Overall, our findings indicate that despite sharing a common genesis and morphology, the mechanical robustness and processability of bijels is strongly mediated by the details of interparticle interactions along the jammed interface, which will be of great significance to the practical use of bijels for advanced materials synthesis. More broadly, in any application of solid-stabilized emulsions involving compositional variations in the liquid phase such as Pickering drug delivery systems, the interfacial tension gradients induced by the payload may cause significant problems for emulsion stability and function. Here we address these issues in the context of bijel processing, but our findings can also be directly applied to the broader class of Pickering systems that involve similar modes of interparticle interactions and interfacial phenomena.
2.4. RESULTS AND DISCUSSION

For critical mixtures of W/L and NM/EG prepared with colloid volume fraction $\phi_p = 0.04$, the storage ($G'$) and loss ($G''$) moduli are monitored over time as the suspensions are quenched from the single-fluid phase to different depths into the two-phase region (Figure 28a and b). The samples show rheological signatures of gelation, with a crossover point where $G'$ becomes consistently larger than $G''$ after the phase boundary is crossed (Figure 28c). In both systems, we observe an increase in the terminal values of $G'$ and $G''$ with deeper quenches, which likely follows from the increase in $\gamma$ and a stronger adsorption of particles at the interface at greater departures from $T_c$. Here the values of $\gamma$ approximately
coincide for W/L samples ramped to \( T = 60 \, ^\circ C \) \( (T-T_c \approx 25 \, ^\circ C) \) and NM/EG samples quenched to \( T = 25 \, ^\circ C \) \( (T_c - T \approx 15 \, ^\circ C) \). However, the elastic modulus was larger for the W/L system by about an order of magnitude. We also note a more prominent aging behavior, as defined by a gradual but continuous growth in the elastic modulus, in the first 15 min after quenching the W/L samples, which slows down considerably by the 30-minute mark. We attribute this behavior to gradual bonding of neighbor particles in a primary van der Waals minimum of the interparticle potential, and will return to this point later on in this chapter. In NM/EG bijels the aging effects were less apparent and \( G' \) did not change significantly once the set temperature had been reached. We therefore used the NM/EG system in another experiment where both the departure temperature, \( (T_c - T) \), and particle volume fraction, \( \phi_p \), were systematically varied to further investigate the origins and hallmarks of viscoelasticity in these systems. It has been theorized that elastic storage in bijels should scale as \( G' \sim \gamma / L_D \), where \( L_D \) is the average width of the fluid domains, determined by the particle loading as \( L_D \sim \phi_p^{-1} \) (ref 24). In addition, for binary fluids close to the critical point, the general relationship \( \gamma (T) \sim (T_c - T)\mu \) has been previously proposed, where \( \mu = 1.26 \) is the standard critical exponent. Experimentally we find that values of \( G' \) when scaled by the product \( \phi_p (T_c - T)\mu \) are more or less constant with no obvious dependence on either \( \phi_p \) or \( T \) (Figure 28d). Our finding supports the idea that stronger bijels may be formed with either 1) an increase in the concentration of stabilizing particles or 2) deeper temperature quenches. It also provides a means for simple quantitative comparison between different systems.
As mentioned earlier, our initial attempts to selectively polymerize NM/EG bijels following the protocol established for the W/L system were unsuccessful; introduction of a monomer typically resulted in mechanical failure of the bijel. Further, the situation was not improved by processing at lower temperatures \(T_c - T = 55^\circ C\) or using samples with higher solids content \(\phi_p = 0.08\). These observations suggest that processability of a bijel is not necessarily directly correlated to the primary determinants of its mechanical integrity, \(\gamma\) and \(L_D\). Inspired by the qualitative differences between the evolutions of \(G'\) in Figure 28a and b, we asked whether a secondary effect such as particle interactions at the interface could play a role. W/L bijels are known to exhibit a fascinating transition in the first minutes after formation, where short-range van der Waals attraction between particles coupled with long-range electrostatic repulsion between charged surface groups induce particle bonding at the interface after an initial annealing period. The resultant bijel variant is known as a “monogel”, and here the particles are no longer held in place by interfacial tension alone and remain assembled as a percolating monolayer even when the fluids are re-mixed. This transition could potentially explain the more prominent aging behavior of the W/L bijels in Figure 28a. We used confocal microscopy to visualize bijels as their fluid constituents were re-mixed, after a 20-min aging period in the jammed state. For the NM/EG system, the structure disintegrates upon raising the temperature above \(T_c\) and the scaffold is re-dispersed as primary particles and/or small clusters in the single fluid phase (Figure 29a). Even for aging periods over 24 h, the particles did not remain assembled at the interface after removing the interfacial tension. In contrast, the jammed particle monolayer in W/L bijels remains intact with little or no change to the morphology as the liquid/liquid interface is removed (Figure 29b). In this series the image contrast is
visibly reduced over time as the fluids re-mix and the refractive index mismatch between the fluid domains is removed.

![Image of fluorescence confocal microscopy images](image)

**FIGURE 29.** TIME SERIES OF FLUORESCENCE CONFOCAL MICROSCOPY IMAGES SHOWING THE BEHAVIOR OF (A) NM/EG BIJELS AND (B) W/L BIJELS AS THE LIQUIDS REMIX (I.E. THE INTERFACIAL TENSION IS REMOVED).

To quantify these observations, we repeated the above experiments on the rheometer and monitored the storage and loss moduli, as the fluids were re-mixed after a 20-minute aging period. As expected, the NM/EG bijel loses its gel-like character upon transitioning to the single-phase region, with $G'$ and $G''$ both falling below the instrument's sensitivity limit (Figure 30a). For the W/L system, the moduli both drop significantly after the interfacial tension is removed; however, gel-like character ($G' > G''$) is retained (Figure 30b), which is consistent with the monogel transition observed in Figure 29b. Further, when the monogel is subsequently broken by shearing at $\gamma = 800 \text{ s}^{-1}$, the particles do not re-aggregate and a liquid-like suspension is instead formed. This result underlines the
essential role played by the temporary particle scaffold during monogel formation, which was predicted at the time of its initial discovery but not observed until now\textsuperscript{75}. The behavior can be contrasted to conventional colloidal gels, which typically return to a gelled state after shearing ceases.

**Figure 30. Rheological Transitions Observed in Bijels of (A) NM/EG and (B) W/L as the Liquids Remix (I.E. The Interfacial Tension Is Removed).**

Collectively, the microscopy and rheology experiments shown in Figure 29 and Figure 30 reveal markedly different behaviors in W/L and NM/EG bijels as the interfacial
tension is removed, and we suspect that this distinction is highly relevant to bijel processing in the two systems. As mentioned earlier, the selective polymerization of W/L bijels is particularly robust; the system is compatible with 10 different monomers at present though this catalog is perpetually expanding, as seen in Table 1.

<table>
<thead>
<tr>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,6-hexanediol diacrylate</td>
</tr>
<tr>
<td>Ethoxylated bisphenol A diacrylate</td>
</tr>
<tr>
<td>Propoxylated glyceryl triacrylate</td>
</tr>
<tr>
<td>Ethoxylated trimethylolpropane triacrylate</td>
</tr>
<tr>
<td>2-phenoxyethyl acrylate</td>
</tr>
<tr>
<td>Dipentaerythritol pentaacrylate</td>
</tr>
<tr>
<td>Poly(ethylene glycol) diacrylate (Mw ~ 258)</td>
</tr>
<tr>
<td>Poly(ethylene glycol) diacrylate (Mw~600)</td>
</tr>
<tr>
<td>Tri(propylene glycol) diacrylate</td>
</tr>
</tbody>
</table>

*TABLE 1. LIST OF MONOMERS THAT HAVE SUCCESSFULLY BEEN USED TO SELECTIVELY POLYMERIZE W/L BIJELS.*

We infer that this flexibility is associated with the possibility of a monogel transition in the W/L system, considering that any of these same monomers tend to destroy the microstructure in NM/EG bijels. To illustrate these differences, we processed bijels in both systems by exposing their surfaces to reservoirs containing pure trimethylol propane triacrylate (TMPTA) and poly(ethylene glycol) diacrylate (PEGDA). In the W/L system, these monomers selectively partition into the lutidine-rich phase and the bijel is transformed into a bicontinuous macroporous solid while preserving the spinodal microstructure (Figure 31). By contrast, the NM/EG bijels gradually collapse by contact
with either monomer, despite the fact that both selectively partition into the NM-rich phase and lead to an overall increase in the interfacial tension between the fluid phases (+11.7% for TMPTA, +4.3% for PEGDA at 9% v/v, 25°C); hence bijel breakdown cannot simply be attributed to an increase in fluid miscibility or decrease in interfacial tension. We recognize that any significant perturbation of the local fluid composition can induce this undesired transition in the NM/EG system, even with the introduction of simple solvents like water or toluene. A possible explanation for this behavior is that the addition of a third component to the bijel microstructure results in a gradient of the liquid interfacial tension along the particle-laden interface and associated Marangoni stresses that can rupture the fluid domains in the absence of a sufficiently rigid particle network. Another possibility is that a substantial change in the fluid composition could alter the 3-phase contact angle of the particles sufficiently such that they detach from the interface. These issues appear to be inconsequential for processing of W/L bijels, where the particles supposedly become trapped in a primary energy minimum upon monogel formation and can conceivably resist structural rearrangements to a greater extent. For example, if the collapse of NM/EG bijels is due to a change in the contact angle, it is not surprising that a monogel-forming system can withstand this change. Similarly, bonding of particles in a primary minimum can provide resistance against tangential surface stresses and impart mechanical stability to the bijel backbone during solvent exchange. Therefore, we believe that the robustness of the W/L system for materials processing is fundamentally correlated to its ability for monogel formation.
All the same, the NM/EG mixture has several advantages over W/L and it is desirable to use this system for bijel processing. Drawing from our findings regarding the sensitivity of NM/EG bijels to steep gradients in composition, we are able to successfully polymerize this system using a reservoir of PEGDA diluted to 20% v/v with nitromethane (Figure 32). Using this strategy allowed the chemical composition of the fluid channels to be more gradually and subtly altered while preventing damage to the 3D spinodal microstructure. Similar to the W/L samples, the polymerized PEGDA scaffold retained the bicontinuous morphology of its bijel parent. These macroporous hydrogels could be valuable in cell and tissue engineering applications where biocompatible scaffolds with large, continuous pores are often desired to improve cell motility and transport of nutrients throughout the microstructure\textsuperscript{76,77}. Our attempts to substantially increase the PEGDA concentration in the reservoir or to use TMPTA in any amount necessary for sufficient crosslinking both led to the destruction of the bijel, which again highlights the sensitivity of
this system to steep gradients in the chemical composition of either fluid phase. We note that while minimizing chemical gradients enables selective polymerization of NM/EG bijels, the process is significantly less flexible and reliable. Additionally, the time required for the monomer to traverse through the bijel microstructure is significantly longer (≈3 h for W/L bijels and 3 days for NM/EG bijels of the same volume and domain size). Nevertheless, our findings demonstrate that monogel formation is not strictly necessary for bijel processing, since we were able to successfully polymerize a NM/EG scaffold (Figure 32), which does not form a monogel (Figure 29a). Though in this chapter we have focused on processing bijels through selective polymerization, the results presented here may have important consequences for any application where foreign components are introduced into bijels, for example in the controlled cross-flow of fluids for chemical reaction or extraction purposes. Overall it appears that particle attraction at the interface can strongly influence bijel rheology and functionality, and the ability to tune these interactions will be invaluable as other applications are developed for these soft materials.
A remaining question is why the monogel transition readily occurs in W/L but not in NM/EG systems. Previous studies have ascribed monogel formation to the bonding of particles in a primary van der Waals minimum. In the W/L system, attractive capillary forces and interfacial jamming drive the particles across a relatively weak electrostatic energy barrier into their primary van der Waals minimum, resulting in particle bonding and hence a robust monogel. In this system, the repulsive barrier only stems from the dissociation of unreacted silanol groups, endowing the particles with a weak, negative electrostatic charge. Considering the similarities in material properties (interfacial tension, dielectric constants, particle core chemistry) between the two systems, it is reasonable to assume that the same modes of attraction operate in the NM/EG system (i.e., van der Waals, capillary, and interfacial jamming), with comparable magnitudes. The different colloid surface chemistries used for the two binary fluid systems must then, directly or indirectly, give rise to the changes in bonding behavior. We hypothesize that the particles
experience a larger repulsive barrier in the NM/EG system, impeding their bonding in a primary van der Waals minimum and thereby inhibiting monogel formation. This larger barrier may originate from solvation of the HMDS graft layer by deprotonated nitromethane molecules, which also contributes negative electrostatic charges to the particles. Based on the observed fragility of the interfacial scaffold in the NM/EG system, the combined dissociation/solvation barrier succeeds in keeping the particles apart, thereby preventing a monogel transition in the NM/EG bijel.

2.5. SUMMARY

In summary, we have used rheology and microscopy studies to investigate the origins of viscoelasticity in bijels and identify key factors that influence their functionality as soft templates for advanced materials synthesis. We observed that both particle loading and the departure from criticality govern the elastic storage modulus in bijels, and that robust bijel processing is presumably linked to attractive interactions between particles at the interface. In the absence of monogel formation, the particle-stabilized interface is more easily disrupted with the incorporation of foreign fluid species, leading to breakdown of the microstructure. Despite this increased sensitivity, we have extended our processing capabilities to the NM/EG system and synthesized bicontinuous, macroporous hydrogel scaffolds for potential use in cell and tissue engineering applications. Finally, our ability to study the rheology of these unique soft materials will enable future research on the fundamental properties of bijels and the influence of particle interactions on their flow properties.
3. BIJEL REINFORCEMENT BY DROPLET BRIDGING: A ROUTE TO BICONTINUOUS MATERIALS WITH LARGE DOMAINS

3.1. BACKGROUND

The unique morphologies of bijels are desirous in many technological applications including tissue engineering\textsuperscript{76,77}, catalysis\textsuperscript{78,79}, electrochemical systems\textsuperscript{20,80,81}, and separation processes\textsuperscript{82,83}. Bijels have also been envisioned as cross-flow microreactors due to the interpenetrating configuration of their constituent phases\textsuperscript{51}. For each of these applications, control over the bijel microstructure and particularly the characteristic domain size, $\xi$ (see Figure 34b), is crucial, as this parameter sets both the pore diameter and the contact area between the different phases in the spinodal-like composites derived from bijels.

As described previously, bijels are the product of a non-equilibrium jamming transition in a complex multiphase mixture. Therefore, a host of physicochemical parameters can influence their formation pathway and the resultant morphology. Most importantly, the amount of solids loading pinpoints the onset of structural arrest during spinodal decomposition, and therefore the colloid volume fraction, $\phi$, can be utilized to influence this transition and tune $\xi$ in bijels. With the spinodal surface uniquely quantified by its single characteristic length scale $\xi$, and a jammed monolayer of particles covering the interface, the relationship $\xi = (\pi/\sqrt{3})(d/\phi)$ is expected in these systems. The scaling of $\xi \sim 1/\phi$ has been experimentally verified for $0.01 < \phi < 0.04$, with a maximum documented domain size of approximately 100 $\mu$m\textsuperscript{51}. This upper limit in $\xi$ has not been explained, but is probably due to gravitational breakdown of the multi-phase mixture at large $\xi$ (small $\phi$).
Presumably, under these conditions the jammed particle monolayer does not impart sufficient mechanical strength to withstand the gravitational forces that act to separate the large interpenetrating liquid domains with disparate densities. Therefore, the upper bound on $\xi$ may have stemmed from a correlation between $\phi$ and bijel rheology, but this important relationship has so far remained unexplored. Understanding this correlation will have important implications for the technological uses of bijels. First, access to domain sizes greater than 100 $\mu$m will be imperative for various applications of bijels including tissue engineering and synthesis of co-continuous composites via nanoparticle infiltration of a porous scaffold. The hypothesis outlined above suggests that in order to successfully create such structures, the bijel must be able to withstand gravitational forces at these large values of $\xi$. Second, as shown in Chapter 2, the ability to transform bijels into bicontinuous porous constructs is also correlated with their rheology. Apparently, bijels must also be able to withstand Marangoni forces along the jammed interface during a liquid exchange step that is required for their processing. Therefore, the rheology of bijels plays an important role in their technological utility, and a better understanding of its relationship with particle volume fraction is needed to advance the applications of this unique and promising class of soft materials.

The wetting properties of the colloidal particles are also of great importance in bijel formation. These properties are characterized by the three-phase contact angle, $\theta$, which describes the equilibrium position of a particle with respect to a fluid–fluid interface (typically measured through the aqueous phase), and is governed by Young’s equation. Such properties also influence the adsorption energy of a particle at the interface,
\[ \Delta G = \pi r^2 \gamma (1 - |\cos \theta|)^2 \]

which, for a sub-micron colloid with near-neutral wetting properties in a binary liquid mixture with \( \gamma \sim 0.8 \) mN m\(^{-1}\), can be several orders of magnitude larger than the particle thermal energy, \( kT \). Here, \( \gamma \) is the interfacial tension, \( r \) is the particle radius, \( \theta \) is the three-phase contact angle, \( T \) is the absolute temperature, and \( k \) is Boltzmann’s constant. Bijel formation necessitates near-neutral wetting properties for the particles (\( \theta \approx 90^\circ \)) to ensure their irreversible adsorption at the interface upon phase separation, which then leads to jamming and mechanical stability in the bicontinuous structure. In this chapter, by tuning the colloid wetting properties, we demonstrate a new class of bijels in which the partitioning of a subset of particles into one of the fluid phases results in secondary droplet bridging and the extension of the colloid network into the fluid domain. For clarity, from hereon we will refer to the systems with and without bridging as bridged bijels and simple bijels, respectively. By characterizing the rheology of simple bijels and their bridged counterparts as a function of \( \phi \), we show that droplet bridging also provides mechanical reinforcement to the particle-jammed scaffold, offering access to bicontinuous structures with \( \xi \) values up to 450 \( \mu \)m, more than four times larger than the previously accessible limit. We postulate a mechanism for this intriguing phenomenon and suggest possible directions for future research in this field. Therefore, this chapter makes the following contributions toward a better general understanding of the kinetic pathways and rheology of interfacially jammed multiphase systems, and particularly bijels:

- Introduction of bridged bijels, a rich and complex multiphase system in which a bicontinuous spinodal-like structure is mechanically stabilized by a combination of interfacial jamming at the spinodal interface and droplet bridging in one fluid phase. This
system not only introduces new intriguing observations and challenging questions for future research, but also provides a route to significantly expand the accessible range of the domain size in bijels.

- Characterization of simple and bridged bijel rheology as a function of the colloid volume fraction, uncovering a universal exponential dependence of the zero-shear elastic modulus, $G'_0$, on $\phi$ in both systems, and new strategies to tune the rheology of these solid-stabilized multiphase mixtures.

Each of the above findings also offers original scientific questions and outlines new directions for future research, which will be presented as we discuss the results.

3.2. EXPERIMENTAL METHODS

3.2.1. PARTICLE SYNTHESIS

Two types of fluorescent silica particles with an average diameter $<d> = 420$ nm and a coefficient of variation CV = 5.1% were used in this study, both prepared following the Stöber method\textsuperscript{69,70}. The dye was prepared by the addition of 12.5 mg of rhodamine B isothiocyanate dye (RITC, Sigma-Aldrich) to a solution containing 10 mL of anhydrous ethanol and 50 mg of 3-aminopropyltriethoxysilane (APS, ≥98%, Sigma-Aldrich) and stirred overnight. The particles were synthesized by adding 10 mL of ammonia (34% w/w, Fisher), 5 mL of the dye solution, and 4.18 mL of tetraethylorthosilicate (TEOS, ≥99%, Sigma-Aldrich) to 35 mL of anhydrous ethanol, and allowing the reaction to proceed overnight. The colloid surface chemistry was further modified in one of two ways. For the particles used in the formation of simple bijels, 3.5 mL of hexamethydisilazane (HMDS, 98%, Alfa Aesar) was directly added to the reaction mixture 3 hours after the addition of
TEOS to render the surface chemistry of particles partially hydrophobic. The particles were then washed in ethanol, and dried in a vacuum oven at 120°C for 1 hour. This treatment imparted neutral wetting properties to the colloids with respect to the NM/EG fluid mixture. The three-phase contact angle, measured with respect to the EG phase by the immersed droplet method, was approximately 98° for these particles, as shown in Figure 33a. For the bridged bijels, the particles were not modified by surface silanization, but washed in deionized water by repeated centrifugation and dried in a vacuum oven at 120°C for 1 hour. This treatment skewed the colloid surface properties away from neutral wetting conditions (θ ~57° with respect to the EG phase, Figure 33b) with a fraction of particles having partial affinity for the EG-rich phase.

![Figure 33](image)

**FIGURE 33.** MEASUREMENT OF THE THREE-PHASE CONTACT ANGLE BY THE IMMERSED DROPLET METHOD FOR BRIDGED BIJEL PARTICLES (A) AND SIMPLE BIJEL PARTICLES (B). THE BOTTOM SURFACE IS MICROSCOPE SLIDE THAT IS SPIN-COATED WITH THE SILICA PARTICLES.

3.2.2. FORMATION OF SIMPLE AND BRIDGED BIJELS

To create the precursor mixture for both the simple and bridged bijels, nitromethane (NM, ≥99%, Sigma-Aldrich) and ethylene glycol (EG, >95%, Fisher Scientific) were added in critical quantities (x_{NM} = 0.64) to the appropriate mass of one of the dry RITC-labeled silica batches to give the desired particle volume fraction, assuming a density
of 2.02 g/mL for silica. The suspension was then mixed via an ultrasonic probe (Branson Sonifier 250) at a power of 40 W for 30 seconds, which simultaneously heated the mixture past its critical point and dispersed the particles. Finally, the mixture was transferred to capillaries that had been preheated to 55°C (0.40 mm 8.00 mm I.D., Vitrocom) and quickly quenched below the UCST by placing the capillaries on an aluminum block at -10°C.

3.2.3. MICROSCOPY

The mixtures were imaged using an inverted microscope (Axio Observer, Carl Zeiss Microimaging, Inc.) attached to a confocal scanner (Vt-eye, Visitech International), using either a 4x (NA = 0.1), 20x (NA = 0.4), or 100x (NA = 1.4) objective. For the analysis of characteristic domain sizes, 20 domains were measured for each sample (see Figure 34b for an example) and the average and standard deviation were recorded.

To explore the phase separation pathway in the binary fluid mixture, a critical solution of NM and EG devoid of particles was mixed at T ~ 60°C and transferred to a preheated capillary. To allow the phase separation process to be visualized, 0.5 mg of Nile red was added to the mixture. This dye preferentially partitions into the NM-rich phase upon demixing, allowing the two fluid phases to be distinguished from one another. The mixture was placed on the microscope stage, and a heated steel block was used to keep the fluids mixed before imaging. The block was then removed to cool the mixture below the UCST by natural convection in air.

3.2.4. RHEOMETRY

Rheological measurements were performed on a stress-controlled rheometer
MCR301, Anton-Paar) with a sandblasted parallel-plate geometry (d = 24 mm, gap height = 0.3 mm). Simple or bridged bijels were formed on the rheometer stage using an integrated Peltier cooling system operating at the maximum cooling rate of 10°C/min. In addition, a Peltier-temperature-controlled hood was used to ensure uniform temperature throughout the sample as well as to minimize evaporation. The single fluid suspensions (T > UCST) were prepared via the same method as noted earlier, and were transferred to the preheated (55°C) rheometer stage and subsequently presheared at $\dot{\gamma} = 800$ s$^{-1}$ for 30 s to remix the suspension and erase any effects of sample handling and loading on the microstructure. The mixture was then quenched to 25°C on the rheometer and left unperturbed for 400 s at this temperature. Oscillatory strain sweeps ($\gamma = 0.005$–100%) at a constant frequency ($f = 1$ Hz) were then performed to measure the storage and loss moduli of the mixture ($G'$ and $G''$, respectively). The zero-shear elastic modulus, $G'_0$, was extracted from these measurements by averaging $G'$ over the range $0.005\% < \gamma < 0.023\%$, where it was nearly independent of $\gamma$.

3.3. RESULTS AND DISCUSSION

**FIGURE 34. CONFOCAL IMAGES OF A BRIDGED BIJEL AT $\phi = 0.08$. SCALE BARS DENOTE 500, 100 AND 10 $\mu$m FOR A, B, AND C, RESPECTIVELY.**
3.3.1. MICROSTRUCTURE OF BRIDGED BIJELS

Figure 34 displays 2D confocal images of a bridged bijel at $\phi = 0.08$ and three different magnifications. The bright regions are fluid interfaces stabilized by the fluorescent particles. The low-magnification image (Figure 34a) clearly shows the bicontinuous morphology of the system similar to simple bijels (see Figure 12 for images of a simple bijel) confirming that the overall structure is formed via spinodal decomposition. However, one of the continuous domains also contains a dense arrangement of discrete particle-armored droplets (Figure 34b). Further, the high-magnification image (Figure 34c) shows that the droplets are bridged by colloidal monolayers with their neighbors, effectively creating a network of particle-bridged droplets within this phase. This dual morphology is unique to the mixture in which the particles are only washed with deionized water and dried in vacuum prior to use (described as particles for bridged bijels in Section 3.2), and occurs through a complex multi-step process that will be further characterized and discussed below.

![Figure 34](image.png)

**FIGURE 35.** PHASE SEPARATION IN A BINARY MIXTURE OF NM AND EG AT THE CRITICAL COMPOSITION OF $X_{NM} = 0.64$, SHOWING THE EARLY (A), INTERMEDIATE (B), AND LATE (C) STAGES OF DEMIXING. THE SCALE BAR DENOTES 500 µM.
The structure of a bridged bijel bears hallmarks of both spinodal decomposition (the overall bicontinuous morphology seen in Figure 34a) and nucleation and growth (the droplets formed within a fluid domain, seen in (Figure 34c), and suggests that both phase separation mechanisms are at play during its formation. To determine whether this phenomenon is inherent to the fluid mixture itself or due to the presence of colloidal particles, we visualized a particle-free NM/EG critical mixture containing Nile red dye as it was quenched below the UCST. Figure 35 shows representative images of the evolution of this mixture as it undergoes phase separation. The bright regions correspond to the NM-rich phase, in which the dye preferentially partitions. Upon quenching below the UCST, the single-phase solution initially demixes through spinodal decomposition, evident by the formation of bicontinuous fluid domains that coarsen over time (Figure 35a and b). However, the late stages of phase separation reveal the formation of droplets within both fluid domains (development of both dark drops (EG) inside of the bright phase (NM) and bright drops inside of the dark phase) in what appears to be secondary nucleation and growth during the demixing process. Tanaka and Araki have previously reported and explored a similar phenomenon in 1D and 2D systems using numerical simulations. They have suggested that two-step demixing in critical mixtures either stems from a competition between hydrodynamic coarsening and diffusion, or is the consequence of a finite quench speed. Briefly, the first effect is seen when rapid hydrodynamic coarsening outpaces molecular diffusion to establish chemical equilibrium, creating a “double quench” effect. The second, and more probable mechanism for the behavior observed here originates from a finite quench speed, which can lead to secondary demixing within each of the already-separated fluid phases. To better illustrate this effect, Figure 36 schematically shows the
NM/EG phase diagram with a representative pathway for two-step demixing marked as I. The initial temperature quench initiates spinodal decomposition in the mixture, quickly separating it into points a and b shown on the diagram. However, continued cooling quenches both points into the binodal (nucleation and growth) region of the phase diagram, and induces secondary demixing in each phase. Based on this argument, we hypothesize that the mechanism for the formation of bridged bijels likely involves a double demixing process that is inherent to the finite-speed temperature quench in the experiments.

![Diagram](image)

**FIGURE 36. SCHEMATIC PHASE DIAGRAM FOR THE NM/EG MIXTURE, SHOWING THE DIFFERENT QUENCH PATHWAYS EMPLOYED IN THIS STUDY. (I) PROPOSED PATHWAY FOR THE FORMATION OF BRIDGED BIJELS THROUGH COMBINED SPINODAL DECOMPOSITION AND NUCLEATION AND GROWTH. (II) OFF-CRITICAL QUENCH IN A NM-RICH MIXTURE. (III) OFF-CRITICAL QUENCH IN AN EG-RICH SAMPLE.**

Secondary phase separation has been previously reported to occur in both bijels and polymeric bicontinuous microemulsions. In particular, in their first experimental realization of bijels using the W/L system, Herzig and coworkers noted that particle stabilized droplets will become increasingly apparent when the colloids have a slight preference for one fluid phase. However, this only resulted in sparse droplets within one fluid domain, which is quite different from the scenario seen in Figure 34. The
polydispersity in the colloid wetting properties, together with the two-step demixing process is responsible for droplet stabilization in both cases. However, in our system, the droplets have been bridged together by the colloids, forming a high-internal-phase solid-stabilized emulsion within one fluid domain, and also extending the particle network from the spinodal boundaries into this phase. As will be discussed below, the formation of such a structure in this system is a highly nontrivial phenomenon, and would require an additional step of molecular exchange across the spinodal interface to effectively invert the compositions of the two fluid phases.

![Diagram](image)

**Figure 36. Proposed Mechanism for the formation of bridged bijels in a critical NM–EG mixture.** (A) Starting point: The particles are loosely flocculated in the single-phase liquid mixture. (B) Early stage: The fluids demix by spinodal decomposition, and the particles partition between the spinodal surface and the EG-rich phase. (C) Late stage: Droplets form by secondary nucleation, and are stabilized in the EG-rich phase by the colloids. (D) Final stage: A network of colloid-bridged droplets is formed within one continuous domain, aided by molecular exchange across the spinodal surface. Bridging of each NM-rich droplet pair occurs across a thin film of the EG-rich phase.

In a recent paper, Lee et al. investigated the conditions for, and the properties of, solid-stabilized emulsions formed by droplet bridging\(^{32}\). They showed that colloids with a slight affinity for the continuous phase in a solid-stabilized emulsion can protrude from the
interface to form a bridge between neighboring droplets. This thermodynamically preferred configuration allows the particle to realize its equilibrium contact angle on both sides, further reducing the interfacial contact between the fluids (and the system’s free energy). Droplet bridging can also lead to gel-like viscoelasticity in these multiphase systems when the particle-bridged network percolates throughout the sample volume. Both aspects of particle-bridged emulsions will be important in interpreting the results seen here. To help discuss the kinetic pathway to bridged bijels, Figure 36 schematically shows our proposed mechanism for their formation. Imaging the starting mixture, we have observed that the silica particles are initially dispersed in a loosely flocculated state in the single-phase mixture. This starting point is schematically represented in Figure 36a. Recall that the colloid wetting properties have been tuned such that upon spinodal decomposition, a subset of particles adheres to the NM/EG interface and the rest of the colloids partition into the EG-rich phase (Figure 36b). The finite temperature quench then leads to secondary phase separation as discussed above, and the particles within the EG-rich phase adsorb to the newfound fluid interfaces (Figure 36c). Note that the surface tension at the secondary droplet interfaces will be greater than the initial spinodal surface, because the droplets are formed through a deeper temperature quench and a wider compositional separation between the corresponding fluid phases (see pathway I in Figure 35). This provides an additional energetic incentive for interfacial colloid adsorption, and explains why particles that do not adhere to the initial spinodal interface adsorb to the droplet surfaces in the EG-rich phase. Particle adsorption also results in droplet bridging (Figure 36d), which is conceivable given the slight affinity of the colloids for the EG-rich phase in this system. However, droplet bridging alone is not sufficient to produce the high-
internal-phase emulsion seen in Figure 34c. As shown in Figure 36, in order to form such a structure, the two fluid phases must nearly invert their compositions (final compositions are depicted in Figure 34b and c), possibly through molecular exchange across the spinodal interface. To our knowledge, this is the first observation of this intriguing phenomenon. We postulate that the droplet stabilization and bridging that occurs in the EG-rich phase transforms the mixture’s energy landscape, providing a thermodynamic driving force for this molecular diffusion. In other words, with colloids present to stabilize and bridge the newly formed droplets, the minimum-energy configuration becomes one in which the particle-laden domains turn into a high-internal-phase emulsion. To further test our hypothesis, we performed off-critical quench experiments at both NM-rich and EG-rich compositions, as depicted in Figure 35 as pathways II and III, respectively. Figure 37 displays confocal images of the NM-rich (Figure 37a, corresponding to pathway II) and EG-rich (Figure 37b, corresponding to pathway III) samples. Note that each of these mixtures itself will separate into a NM-rich and an EG-rich phase upon cooling, but the volumes and morphologies of the two phases will be different between the samples. Two important observations about these images corroborate our hypothesis outlined above. First, the NM-rich quench (pathway II) results in a mixture that is primarily comprised of particle-free regions (black areas in Figure 37a) with sparsely dispersed particle-filled domains (bright areas in Figure 37a). Conversely, the EG-rich quench (pathway III) results in the opposite: sparse voids within a particle-filled sea of fluid. This confirms that the colloids selectively partition into the EG-rich phase upon demixing. Second, the EG-rich phase itself turns into a dense colloid-stabilized emulsion in both cases. It is difficult to discern the detailed morphology of the particle-bourn regions in the NM-rich sample (Figure 37a), but droplet
bridging appears to have occurred in the EG-rich mixture (Figure 37b). This finding supports the notion of secondary phase separation due to a finite quench speed being responsible for droplet formation in bridged bijels. This is because the interface quench mechanism, which stems from a competition between hydrodynamic coarsening and molecular diffusion, can only occur when phase separation is initiated by spinodal decomposition\textsuperscript{88}. Here, off-critical demixing proceeds exclusively through nucleation and growth, which does not involve hydrodynamic coarsening. Therefore, the presence of secondary droplets cannot be due to an interface quench effect, and corroborates our hypothesis of a double-phase separation mechanism due to a finite quench speed in our experiments.

Our experiments reveal a new class of solid-stabilized emulsions with hierarchical morphology assembled through a multi-step phase separation process. Our analysis provides the first glimpse into the microstructure and formation mechanism of these multi-phase systems. We hope that the findings presented above will motivate and trigger future theoretical studies to better elucidate the kinetic pathways leading to the formation of these complex multi-phase microstructures.
FIGURE 37. CONFOCAL IMAGES OF OFF-CRITICAL SAMPLES QUENCHED INTO THE UNSTABLE REGION IN THE PRESENCE OF COLLOIDAL PARTICLES. (A) NM-RICH SAMPLE, (B) EG-RICH SAMPLE. SCALE BARS DENOTE 500 µM FOR THE MAIN IMAGES AND 30 µM FOR THE INSETS.

3.3.2. ACCESSIBLE RANGE OF $\xi$

Figure 38 presents the characteristic domain size, $\xi$, plotted against $1/\phi$ for both the simple and bridged bijel systems. In these experiments the colloid volume fraction was varied in the range $0.01 < \phi < 0.12$. A number of important features become apparent in the figure. First, simple bijels show the expected scaling $\xi \sim 1/\phi$ with a slope of 0.81 µm, which is close to the theoretical value of 1.1 µm based on complete monolayer coverage, which gives $\xi = (\pi/\sqrt{3})(d/\phi)$. Second, at any given $\phi$, the domain size in a bridged bijel is considerably larger than its simple bijel counterpart. Third, the smallest value of $\phi$ at which mechanically stable samples can be formed is also lower in bridged bijels ($\phi_{\text{min}} = 0.02$ and 0.01 in simple and bridged bijels, respectively). Collectively, these two effects allow access to significantly larger domains in bridged bijels: the largest accessible values of $\xi$ in simple and bridged bijels are $\xi = 54$ µm at $\phi = 0.02$, and $\xi = 450$ µm at $\phi = 0.01$, respectively.
Another important observation in Figure 38 is the deviation of bridged bijels from a universal linear scaling between $\xi$ and $1/\phi$. We notice an apparent two-regime behavior with two distinct slopes, which are experimentally found to be 10.4 $\mu$m in Regime I, and 4.3 $\mu$m in Regime II, and a crossover between the two regimes at approximately $\phi = 0.04$. The linear scaling within each regime probably stems from the overall spinodal-like morphology of the bridged bijels. However, the dual scaling points to possible morphological differences below and above $\phi \sim 0.04$. To further investigate this behavior, we carefully examined confocal images of bridged bijels within each regime. Representative images from two samples at $\phi = 0.07$ and 0.02 are shown in Figure 39. Upon careful inspection, it is apparent that in Regime I, a network of bridged droplets fills out the entirety of the corresponding fluid domain (Figure 39a), whereas in Regime II, regions within the fluid domain remain devoid of droplets (Figure 39b). These differences could plausibly lead to the dual scaling seen in Figure 38; Regime II is more structurally similar to
a simple bijel due to its droplet-free regions, and shows a less significant deviation from the simple bijel slope. All in all, the combined effect of the larger slopes in the scaling of $\xi$ with $1/\phi$, and the formation of mechanically stable structures at lower $\phi$ in bridged bijels significantly pushes the high-end limit of accessible $\xi$ in these spinodal-like morphologies. As discussed earlier, access to larger domain sizes is advantageous for many technological applications, but cannot be achieved in the simple bijel morphology due to loss of mechanical stability at low $\phi$. Evidently, the secondary nucleation and droplet bridging processes presented above help maintain mechanical stability in the system at large $\xi$. The rheological origins of this phenomenon are further examined next.

![Representative Confocal Images from the Two Regimes Identified in Figure 38](image.png)

**Figure 39.** Representative confocal images from the two regimes identified in Figure 38. (A) Regime I, $\phi = 0.07$; (B) Regime II, $\phi = 0.02$. Scale bars denote 100 μM.

### 3.3.3. Rheology of Bijels

In a recent study, Lee et al. showed that colloid-mediated bridging can lead to the formation of a percolating particle network and impart gel-like rheology in solid-stabilized
emulsions. Therefore, we suspect that droplet-bridging may serve as additional reinforcement for the jammed spinodal interface and contribute to mechanical stability in the system. This viewpoint would explain how bridged bijels offer access to larger domain sizes without loss of mechanical stability. To assess this notion, we performed rheological measurements on both simple and bridged bijels at different particle volume fractions in the range $0.01 < \phi < 0.11$. Figure 40a presents the results of oscillatory strain sweeps at $f = 1$ Hz on these mixtures. Both systems display signatures of gel-like rheology, with solid-like viscoelasticity (plateau in $G'$, with its value at least an order of magnitude larger than $G''$) at small $\gamma$, and an apparent yield stress (precipitous drop in $G'$ and crossover with $G''$ at a sufficiently large strain or stress). The zero-shear elastic modulus, $G'_0$, extracted from this data as described in Section 3.2, is plotted for both systems as a function of $\phi$ in Figure 40b.

**FIGURE 40. RHEOLOGY OF SIMPLE AND BRIDGED BIJELS.** (A) STRAIN SWEEP PROFILES AT VARIOUS PARTICLE VOLUME FRACTIONS. THE CIRCLES AND SQUARES REPRESENT THE BRIDGED AND SIMPLE BIJELS, AND THE SOLID AND OPEN SYMBOLS REPRESENT $G'$ AND $G''$, RESPECTIVELY. THE VOLUME FRACTION IS DENOTED BY THE COLOR, AS SPECIFIED IN THE CAPTION. (B) SCALING OF THE ZERO-SHEAR ELASTIC MODULUS WITH PARTICLE VOLUME FRACTION FOR SIMPLE AND BRIDGED BIJELS AND DENSE PICKERING EMULSIONS.
For comparison, we also include values of $G'$ from a solid-stabilized (Pickering) emulsions created with the same particles as those used to form the bridged bijels. To recover gel-like viscoelasticity in the Pickering emulsions, we had to increase both $\phi$ and the volume fraction of the dispersed liquid phase, $\eta$, dramatically ($0.10 < \phi < 0.22, \eta = 0.675$). This is because in bijels, interfacial jamming can lead to mechanical stability and gel-like properties at low solids loadings; but in the Pickering emulsions, a densely packed collection of colloid-stabilized droplets is required to achieve the zero-shear solid-like response characterized here (see Figure 41 for a representative confocal image of the Pickering emulsion, showing the dense droplet packing in this system). Qualitatively, as the solids loading is increased, the strength of the gel also increases in all three systems. However, for the bijels, $G'_0$ shows an intriguing exponential dependence on $\phi$—experimentally, the data best fits to the equation $G'_0 \sim \exp(32\phi)$. This is in sharp contrast
with both the densely packed Pickering emulsion, where a linear dependence similar to surfactant-based systems\textsuperscript{93} is observed ($G'_0 \sim 1730\phi$), and the heterogeneous bridged emulsion studied by Lee et al., in which a power-law form similar to colloidal gels ($G'_0 \sim \phi^3$) was reported\textsuperscript{92}. All four systems are comprised of a binary mixture of immiscible liquids and colloids that adsorb to the fluid interfaces. Therefore, their utterly distinct rheological signatures probably stem from their dissimilar microstructures: a minimal-surface spinodal architecture in bijels, a heterogeneous percolating network of adhesive droplets in the bridged emulsion, and a homogeneous, densely packed collection of particle-stabilized droplets in the Pickering emulsion. The exact origin of the exponential dependence in bijels is unclear at this point, but would be an important topic for future research in this area. However, another important observation can also be made from the results of Figure 40. Here, the strain sweep profiles for the simple and bridged bijels at the same $\phi$ (Figure 40a), and the scaling of $G'_0$ with $\phi$ (Figure 40b) are practically indistinguishable between the two systems. Thus, with the scaling dictated by the overall morphology (exponential scaling for spinodal-like structures), the rheological signatures of these systems are apparently determined by $\phi$ alone. Lee et al. also showed a direct correlation between the rheological characteristics and particle volume fraction in bridged emulsions, explaining that the gel-like properties stem from the percolating network of colloidal particles, and the morphology of this network (a heterogeneous collection of clusters and voids in their case) determines the scaling of $G'_0$ with $\phi$. Here, we hypothesize that in both the simple and bridged bijels, the overall percolating path of the jammed particles is defined by the spinodal surface, thus giving rise to the same (exponential) functionality in both systems.
However, in bridged bijels, the particles that participate in bridging inside the fluid domains contribute to mechanical stability in the mixture, but do not partake in interfacial jamming of the spinodal surface, which is the primary determinant of $\xi$. This is precisely why bridged bijels can provide access to much larger values of $\xi$; because their mechanical stability is determined by the entire particle population, but their characteristic domain size is determined only by the fraction of particles that adhere to the initial spinodal surface. These findings reveal new interfacial strategies to tune the rheology of particle-stabilized emulsions, and propose original questions and new phenomena yet to be explored and discovered in these systems. Future research should focus on modeling the interparticle forces in bijels, the origins of the exponential relationship between $G'_0$ and $\phi$, and large-amplitude oscillatory shear experiments, which would further the understanding of bijel rheology and the unique characteristics of minimal-surface structures formed in these multiphase mixtures.

3.4. SUMMARY

We have presented and analyzed the microstructure and rheology of a new solid-stabilized multi-phase system that we term a bridged bijel. This material exhibits an overall bicontinuous morphology similar to a simple bijel, but with one fluid domain filled with bridged liquid droplets. This unique morphology is the result of a combined spinodal decomposition and secondary nucleation-and-growth mechanism in binary liquid mixtures containing interfacially active colloids with partial affinity for one fluid phase. The rheological signatures of bridged bijels are nearly identical to their simple bijel counterparts at the same $\phi$, and both systems show a unique exponential relationship
between \(G'\) and \(\phi\) stemming from their overall spinodal microstructure. However, droplet bridging extends the colloid network from the spinodal interface into one fluid domain and imparts mechanical reinforcement to the scaffold, while partitioning of the colloids between the spinodal surface and the fluid domain delays the onset of structural arrest, providing access to characteristic domain sizes upwards of 450 \(\mu\)m in bridged bijels. Our findings reveal new interfacial phenomena leading to hierarchical multiphase morphologies, and strategies for tuning the rheology of solid-stabilized emulsions and bijels. In addition, the ability to form mechanically stable bicontinuous structures at large \(\xi\) (low \(\phi\)) can extend the applications of these unique materials into new areas such as tissue engineering where domains on the order of hundreds of microns are required for simultaneous nutrient transport and cell growth, or chemical transformations of bijels by nanoparticle infiltration.
4. BIJELS AS TEMPLATES FOR NEXT GENERATION ENERGY STORAGE ELECTRODES

Electrochemical supercapacitors and rechargeable batteries have emerged as promising technologies for advanced energy storage and conversion, but their uses are currently limited by the energy and power densities that they can deliver\textsuperscript{94,95}. Supercapacitors characteristically enjoy high charge/discharge rates and extensive cycle life but suffer from low energy densities, restraining their use to high-power, short duration applications\textsuperscript{10,96}. By contrast, batteries can deliver energy for longer periods but only at reduced rates, making them suitable for low-power applications that demand extended use between charge cycles. The performance of electrodes in batteries and supercapacitors is governed by their chemical makeup and microstructural configuration at the length scales that govern energy storage and charge transport in electrochemical composites\textsuperscript{97}. As mentioned in Section 1.3, the envisioned ideal configuration is one that simultaneously provides percolating passages for electrons and ions to freely flow throughout the structure, minimizes the length and resistance of transport pathways, and enables a large volumetric density of electrolytically active materials\textsuperscript{6,9}. Bicontinuous scaffolds provide a reasonable approach to create this idealized structure, and there have been many attempts to create an optimized microstructure, as will be discussed shortly. However, these designs have not been able to bridge the gap between batteries and supercapacitors in the context of their energy and power densities. Thus, this work aims to introduce a new microstructure (one derived from bijels) that can simultaneously deliver high power and energy, which is afforded by the unique microstructure of bijels.
Emulsion templating is one method to create highly porous scaffolds\textsuperscript{98}. Emulsions, similar to Pickering emulsions described previously, are mixtures of one immiscible fluid that is dispersed in a continuous phase in the form of droplets. These droplets normally have a wide size distribution, but can become monodisperse depending on the processing technique, and typically are at least a few microns in diameter. Through polymerization of the continuous phase (in particular when you have concentrated emulsions), and subsequent removal of the dispersed phase, a high porous, emulsion-templated material is produced (as depicted in Figure 42\textsuperscript{98}).

![Figure 42 SEM Image](image)

**FIGURE 42. SEM IMAGE OF A TYPICAL EMULSION-TEMPLATED POROUS MATERIAL, SCALE BAR DENOTES 5 MICRONS (REPRODUCED FROM REF. 98).**

Lithography, including both multibeam holographic lithography (interference lithography) and phase-shift photolithography, is another promising technique to create 3D microstructured materials. Photolithography offers the ability to create a vast array of geometric patterns using light to transfer a pattern from a photomask to a photoresist, and subsequently processing either etches the pattern or enables deposition of a new material onto the substrate below the photoresist, creating a 3D patterned material\textsuperscript{99}. Interference lithography, on the other hand, is a maskless technique that relies on the interference
pattern of two more light sources that is exposed to a photosensitive layer, creating the desired pattern throughout a 3D sample\textsuperscript{100}. A sample structure created through this technique is shown in Figure 43\textsuperscript{101}.

![Figure 43](image)

**FIGURE 43. SEM IMAGE OF THE LITHOGRAPHICALLY DEFINED MICROSTRUCTURE (REPRODUCED FROM REF. 101).**

Direct ink writing is a technique that creates carefully designed 3D structured materials. This method uses an ink-deposition nozzle along with a computer-controlled stage to create 3D materials with a precisely controlled microstructure\textsuperscript{102}. Many different inks can be used, including polymer melts\textsuperscript{103}, waxes\textsuperscript{104}, and colloidal gels\textsuperscript{105} and suspensions\textsuperscript{106} to name a few. The inks solidify through gelation, temperature liquid-evaporation or solvent-induced phase change\textsuperscript{102}. One such microstructure that can be created through this method is shown in Figure 44\textsuperscript{107}.  

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Recently, Zhang et al. have shown that composite electrodes derived from inverse opal structures can offer rapid charge and discharge rates while maintaining a fairly modest energy density\textsuperscript{20,108}. These architectures are fabricated through creating a 3D colloidal crystal using particles ranging from 100 nm to 2.5 microns, and upon drying is then used as a template for deposition of materials. Materials can be deposited via a range of different methods including electrodeposition, atomic layer deposition and chemical vapor deposition\textsuperscript{109}. Subsequent etching renders a highly porous material of spherical pockets connected by small interstitial windows, as shown in Figure 45\textsuperscript{20}. 

**FIGURE 44. EXAMPLE MICROSTRUCTURE OF A 3D MICROSTRUCTURED MATERIAL CREATED VIA THE DIRECT-INK PRINTING METHOD (REPRODUCED FROM REF. 107).**
FIGURE 45. SEM IMAGES OF THE INVERSE OPAL DESIGN. NOTE THE NON-UNIFORMITY IN THE PORE STRUCTURE, LIMITING THE AMOUNT OF ACTIVE MATERIAL THAT CAN BE DEPOSITED (REPRODUCED FROM REF. 20).

However, the common problem in each of the prior designs is that the morphology does not lend itself to the level of morphological control needed to independently tune the electrode’s capacity and power density while also conserving the required co-continuity to avoid current constriction in the charge carrier transport pathways. In particular, these past designs has at least one of the following drawbacks: 1) non-uniform pore distribution, 2) non-uniform pore geometry and/or 3) a processing technique that limits the overall thickness of the electrode to under \( \sim 15 \) \( \mu m \), restricting the total amount of stored energy in these systems. Non-uniformity in either pore diameter or pore structure limits the amount of electrolytically active material that can be deposited onto the current collector while also ensuring a percolating path for the electrolyte throughout the entire electrode. This chapter aims to address these issues by using bijels as a template to create highly uniform, co-continuous electrodes. Two different chemistries will be presented. Section 4.1 introduces a composite nickel/nickel hydroxide positive electrode that offers the energy density of batteries and the power density of supercapacitors. In Section 4.2, bijels are used a template to create a composite carbon/silicon electrode that can be used as an anode for
Li-ion batteries. Uniquely, the particles used to create the initial bijel scaffold are no longer sacrificial; instead they are integral to the final electrode’s chemical composition. Overall, this chapter presents the first applied use of bijels as functional electrolytically active materials, and demonstrates the enhanced electrochemical characteristics of these electrodes that stem from the unique microstructure of bijels.

4.1. NICKEL/NICKEL HYDROXIDE ELECTRODES

4.1.1. BACKGROUND

Nickel hydroxide \((\text{Ni(OH)}_2)\) has been widely used as a positive electrode active material for both nickel-metal hydride (NiMH)\(^{110}\) and nickel-cadmium(Ni-Cd)\(^{111}\) batteries as well as supercapacitors\(^{112}\). In each of these systems, the reduction and oxidation (redox) reaction taking place is given by\(^{113}\)

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^-.
\]

During charge, nickel hydroxide is oxidized to form nickel oxyhydroxide (NiOOH), and during discharge NiOOH is reduced back to Ni(OH)\(_2\). Moreover, each of these materials have been known to exist in two different crystallographic forms, as shown in Figure 46\(^{114}\). Current NiMH batteries operate under the \(\beta/\beta\) cycle, where discharging of \(\beta\)-NiOOH produces \(\beta\)-Ni(OH)\(_2\), because of it’s stability in the electrolyte (KOH) and the relatively simple manner of keeping the electrode phase pure. The \(\alpha/\gamma\) phases can incorporate water molecules into their structure, are relatively unstable in alkaline medium, and can transform more easily to their \(\beta\) counter part. Thus, it is desirous to synthesize \(\beta\)-Ni(OH)\(_2\) as well as operate the electrode under conditions such that both NiOOH and Ni(OH)\(_2\) stay in
the $\beta$ phase. There has been considerable work focusing on the synthesis of Ni(OH)$_2$, especially focusing on the creating a pure $\beta$ phase$^{115,116}$ as well as making it nanoporous$^{117,118}$. The scope of this work is not to reinvent this synthesis process, but rather to introduce a new manner in which this material can be arranged in a 3D volume. Besides the industrial relevance of this material, it was chosen due to its safety, low cost, and it’s relatively good redox activity. Moreover, there have been many studies on 3D electrodes with nickel hydroxide as the active material, including an inverse opal structure$^{20}$, foams$^{119,120}$, lithography defined microstructures$^{101,121}$, and nanofoams$^{122}$ to name a few.

![Diagram showing phase changes](image)

**Figure 46. Schematic of the phase changes that can occur in both nickel hydroxide and nickel oxyhydroxide during either overcharge or dehydration.**

4.1.2. **Experimental Methods**

4.1.2.1. *Silica Synthesis*

Fluorescent silica particles with an average diameter of 697 nm and coefficient of variation of 2.6% were prepared via a modified Stöber Process and an SEM image of the
obtained particles is shown in Figure 47. The dye was prepared by the addition of 12.5 mg of fluorescein isothiocyanate isomer (FITC) to a 20 mL vial containing 10 mL of anhydrous ethanol and 52.6 μL of 3-aminopropyltriethoxysilane and was stirred overnight. The silica particles were synthesized by the addition of 4.18 mL of tetraethylorthosilicate to a 250 mL flask containing 35 mL of anhydrous ethanol, 10 mL of ammonia, and 5 mL of the prepared dye solution, and allowing the reaction to proceed overnight. The particles were then washed in water by repeated centrifugation, dried in an oven at 70°C for 4 hours, and then transferred to a vacuum oven maintained at 110 °C and allowed to dry for several days to obtain neutrally wetting properties.

![Figure 47. WATER/2,6-LUTIDINE FITC SILICA PARTICLES](image)

4.1.2.2. **Bijel Formation and Processing**

Silica particles were dispersed in Millipore water via an ultrasonic probe at a power of 40 W for 4 minutes, and allowed to cool to room temperature. A known volume of 2,6-lutidine was then added to the silica dispersion to give a near-critical composition with respect to water (x_lut = 0.064). A vortex mixer was used to quickly agitate the sample, and
200 μL of the mixture was added to homemade microscopy vials (5 mm inner diameter cylindrical glass tubes). Bijels were then formed through exposure of the sample to microwave radiation at a power of 95 W for 30 seconds. Samples were transferred to an oven maintained at 70°C and left unperturbed for 30 minutes. Then, 70 μL of 1,6-hexandiol diacrylate monomer mixed with a photoinitiator was carefully placed on top of the sample and allowed to diffuse into the lutidine-rich domains. After 5 hours, the liquid on top of the sample was removed and replaced with fresh monomer solution. After an additional 5 hours, keeping the samples above the critical temperature of 34.1°C, photopolymerization was carried out using an ultraviolet lamp (Omnicure 1000, 40 W) for 80 seconds, producing a bicontinuous polymer sponge with bijel morphology. The silica particles were etched from the internal surfaces using 14.45M hydrofluoric acid.

4.1.2.3. Nickel Shell Fabrication

The polymer template was immersed in a saturated solution of palladium chloride in anhydrous ethanol overnight. An electroless nickel-plating solution composed of 0.02 M nickel chloride hexahydrate, 0.02 M sodium tartrate dehydrate, and 1 M hydrazine was prepared. The pH of the plating bath was adjusted to 10 using sodium hydroxide and maintained at a temperature of 95°C for the duration of the plating period (75 minutes). The sample was sintered in air at 300°C for 4 hours and 500°C for 4 hours to completely remove the polymer scaffold. The oxidized nickel sample was then reduced to nickel by sintering under 4% H₂ in Ar for 8 hours at 450°C.
4.1.2.4.  Ni(OH)$_2$ Deposition

The Ni/Ni(OH)$_2$ composite was prepared by a known hydrothermal reaction$^{119}$. Briefly, 32 mg of nickel chloride hexahydrate and 50 mg of urea were added to 20 mL of water, and transferred to an autoclave reactor along with the porous nickel scaffold. The reactor was heated to 180°C for the desired time, and then allowed to cool down to room temperature. The resulting composite electrode was washed with deionized water and isopropyl alcohol, and allowed to dry overnight at 70°C.

4.1.2.5.  Characterization

Scanning electron microscopy was performed using a FEI Quanta 3D FEG Dual Beam microscope. All X-Ray Diffraction experiments were conducted using a Rigaku SmartLab. Electrochemical characterization and tests were done using a Solartron CellTest System Model 1470E controlled by CorrWare software. All materials were weighed using a Radwag MYA 2.3Y microbalance with 1 mg readability. The XRD pattern of the nickel shell after being sintered in air is shown in Figure 48a. The pattern can be indexed to JCPDS card #22-1189 (nickel oxide) and JCPDS card # 01-078-07533 (nickel), clearly showing that some of the nickel is oxidized to NiO when sintered under air. In order to reduce the NiO to nickel, the sample was reduced under H$_2$ (4% in Ar). The XRD pattern of this step (Figure 48b) can be indexed to JCPDS card # 01-078-7533 (nickel), showing that all the nickel oxide was reduced to nickel. Finally, the XRD pattern of free particles formed during the CBD of the nickel hydroxide formation is shown in Figure 48c, and can be indexed to JCPDS card #14-0117 (β-Nickel Hydroxide).
4.1.3. RESULTS

Advances toward the ideal electrode morphology can only be achieved through co-continuous microstructured composites with highly controllable and uniform internal domains. Such characteristics are uniquely met in a new class of soft materials known as bicontinuous interfacially jammed emulsion gels (bijels)\(^{24}\). As described earlier, bijels are formed through arrested phase separation in a binary liquid mixture undergoing spinodal decomposition in the presence of neutrally wetting colloidal particles\(^{51}\). During phase separation, the particles sequester to the fluid-fluid interface and become jammed once the interfacial area is sufficiently reduced to just accommodate them. The resulting non-equilibrium material consists of two uniform, interpenetrating and continuous fluid domains separated by a colloid monolayer. Importantly, the characteristic domain size in these dynamically self-similar systems, herein denoted as \(\xi\), is directly related to the internal surface area per unit volume, \(S_v\), and can be tuned through the colloid volume fraction and wetting properties\(^{55}\). Through post-processing techniques recently pioneered in our laboratory, these soft materials can be converted into macroporous and
hierarchically porous metals, ceramics, and polymers with tunable pore size
distributions. Building on these developments, here we utilize bijels as soft matter
templates for the synthesis of three-dimensional, co-continuous composite electrodes for
electrochemical energy storage and conversion. Our method uniquely allows us to
independently tune two important microstructural parameters that govern the
electrochemical performance of these systems, establishing the bridge between
supercapacitors and batteries with electrodes that simultaneously offer tunable, and large,
power and energy densities.

As seen in Figure 49, our electrodes are comprised of three independently
percolating phases: (a) a nickel backbone, which serves as the current collector, (b) a thin
coating of Ni(OH)₂ as the electrolytically active phase, and (c) an electrolyte solution of 6 M
KOH that fills the remaining voids. Ni(OH)₂ chemistry was used here due to its relevance to
electrochemical supercapacitors and batteries, low cost, relative safety, and well-known
electrochemical characteristics. Using bijel templates for this process offers the following
critical advantages: (1) uniform pore geometry, allowing for efficient ion transport to
electrochemically active sites throughout the entire structure, (2) the ability to tune the
internal surface area during bijel formation, and (3) the ability to independently adjust the active material thickness. Collectively, these control knobs enable microstructural optimization of the composite electrodes to simultaneously deliver high energy and power densities, both on a gravimetric and volumetric basis. In particular, the unique morphology of our bijel-derived composites combines a thin coating of active material with a large internal surface area and efficient ion transport paths through the electrolyte phase while maintaining co-continuity of all phases to provide both rapid charge/discharge kinetics and a large capacity for energy storage.

**FIGURE 50. MICROSTRUCTURE OF THE COMPOSITE ELECTRODE.** (A-C) BARE NICKEL SHELLS WITH 8 µM, 15 µM AND 22 µM DOMAINS. (D-F) THE 15 µM ELECTRODE WITH THREE DIFFERENT ACTIVE MATERIAL THICKNESSES OF 475 nM, 675 µM, AND 1 µM. THE SCALE BARS DENOTE 25 µM FOR (1-C), 10 µM FOR (D-F), AND 1 µM FOR THE INSETS IN (D-F).
The Ni/Ni(OH)$_2$ composite electrodes were synthesized by simple chemical processing of bijel templates. Bijels were prepared by spinodal decomposition in a binary mixture of 2,6-lutidine and water, and arrested by interfacial jamming of colloidal silica particles 697 nm in diameter with a coefficient of variance of 2.6%$^{51}$. The colloid volume fraction was varied from 0.014 to 0.040 to adjust the characteristic domain size, $\xi$. Bijels were transformed into bicontinuous polymer scaffolds by selectively polymerizing the lutidine phase with a hydrophobic monomer (1,6 hexanedioldiacrylate) mixed with a photoinitiator (Darocur 1173)$^{57}$. Nickel was then electrolessly deposited on the polymer scaffold to create a 1 $\mu$m thick coating on the outer surface of the polymer. The coated samples were sintered at 500°C in air to completely remove the polymer, and subsequently sintered at 450°C under H$_2$ (4% in Ar) to ensure the formation of pure nickel, as seen in Figure 48. The resulting morphology, shown in Figure 50a-c, is a highly porous nickel shell with uniform, continuous pores tuned in the range 8 $\mu$m $< \xi < 22 \mu$m. Ni(OH)$_2$ was deposited on the nickel shell by chemical bath deposition, creating the final composite electrode consisting of a conductive backbone coated with a thin layer of an electrolytically active material, and a continuous void phase. By controlling the deposition time, the active layer thickness, herein denoted as $\delta$, was varied ($\delta = 475$ nm, 675 nm, and 1 $\mu$m), as shown in Figure 50d-f. Therefore, we created an array of electrodes with varying active material thicknesses and electrolyte pore sizes, exemplifying the versatility in this fabrication technique. The electrodes will herein be referred to by their pore diameter in $\mu$m followed by the active coating thickness in nm, in the $\xi/\delta$ format (for example, 22/675 refers to the electrode with 22 $\mu$m pores and an active layer thickness of 675 nm).
Electrochemical characterization of the composites was performed using a three-electrode setup with a Pt wire counter electrode, Ag/AgCl reference electrode, and 6 M KOH electrolyte. As a representative example, cyclic voltammetry (CV) curves at varying scan rates for the 22/675 composite are shown in Figure 51a. Each CV curve displays two...
clear peaks corresponding to the oxidation and reduction of the active material in the reversible reaction Ni(OH)$_2$ ↔ NiOOH + H$^+$ + e$^-$ (ref. 113). A control experiment was performed on a bare nickel shell, and the resulting faradaic peaks were almost undetectable (Figure 52), confirming that the electrochemical performance predominantly originates from the electrolytically active material alone. Additionally, the 22/675 electrode was synthesized and tested four times to determine the reproducibility of our technique. Figure 53 shows the average specific capacitance values calculated from both discharge tests and CV curves for these four electrodes, and clearly displays the reproducibility in our processing technique.

![Figure 52. CV Plot of the 22/675 Ni/Ni(OH)$_2$ Composite Electrode (Solid Line) and a Pure Nickel Shell (Dashed Line) at a Scan Rate of 25 mV/S.](image-url)
Clear redox peaks were still apparent at scan rates up to 250 mV/s, indicating the high-rate capability of this electrode. Specific capacitances were calculated from the discharge curves shown in Figure 51c, and a maximum gravimetric capacitance of 2148.5 F/g was achieved at a current density of 1 A/g, close to the theoretical value of 2305 F/g. Increasing the current density by an order of magnitude (from 1 to 10 A/g) decreased the gravimetric capacitance by only 6%, compared to a typical decrease of 30% or more in most of the published work on Ni(OH)$_2$ based electrodes$^{119,123,124}$. Even at an outstanding current density of 250 A/g, the specific capacitance showed a decrease of only 39% (to 1310 F/g) from its maximum value, demonstrating the efficient use of active material in our bijel-based electrodes even at exceedingly large current densities. The corresponding CV and discharge curves for the other electrodes are presented in Appendix 6.1, and show similar behavior as the 22/675 specimen. Therefore, our bijel-derived composites characteristically enable high current delivery with minimal loss in specific capacitance,
which stems from the unique way in which the active material is organized within the structure (in particular, its arrangement as a thin shell and accessibility throughout the volume).

To determine the long-term stability of our electrodes, the 22/675 specimen was tested at a current density of 25 A/g for 1000 cycles. As shown in Figure 54a, the electrode demonstrated excellent stability, maintaining at least 80% of its original capacitance throughout the process. Furthermore, Figure 54b shows an SEM images of the sample and reveals that the electrode microstructure remains intact after the cycling test further corroborating the excellent mechanical stability of our composites.

As mentioned earlier, our method uniquely allows us to independently tune $S_v$ (characterized here through variations in $\xi$) and $\delta$ during the bijel formation and chemical bath deposition steps, respectively. Together, these two morphological parameters govern
the overall electrochemical performance of our system, since $\delta$ controls the length scale for ion transport into the active layer, and the product $S_\nu \delta$ determines the volume fraction of active material. To demonstrate how independent control over these two parameters allows us to tune the electrochemical performance of our bijel-based electrodes, the gravimetric and volumetric energy and power densities of our materials are presented as Ragone plots in Figure 55, and are compared to other systems reported in the literature. The general shape of these graphs shows a roughly constant energy density until a critical power density is reached, which is presumably the point at which ion diffusion through the active layer begins to limit the electrode’s performance. As seen in Figure 55a, this critical specific power is correlated directly with $\delta$, independent of the value of $\xi$. Therefore, discharge kinetics and power density can be tuned in our systems through the active material thickness. In addition, each electrode reaches roughly the same specific energy (178±8 Wh/kg) at low specific power, indicating that our co-continuous design enables usage of the entirety of the active material. The 15/475 electrode performed the best, achieving a maximum specific power of 270 kW/kg while preserving a modest specific energy (34.3 Wh/kg). On a gravimetric basis, we match or exceed the best values reported in the literature, providing at least $2\times$ the energy density at comparable specific powers for 3 out of the 4 reported values$^{123,125-127}$. This is again afforded by the unique architecture of our electrode, which allows for rapid energy delivery to and from the entirety of the active material, enabling battery-type specific energies and rate performances equivalent to or surpassing that of the best supercapacitors.
As discussed above, the superior specific power achieved in the 15/475 electrode is likely due to the small thickness of $\delta$, providing a short diffusion path for ion transport through this layer. While this general strategy has already been employed in porous electrochemical composites by previous researchers, the entire electrode thickness has been purposely kept under 15 µm to ameliorate ion transport limitations into the tortuous pores, or due to constraints with the fabrication techniques implemented$^{108,128}$. This approach then imposes a limit on the total amount of energy that can be stored in the cell. By contrast, the uniform, continuous pore morphology in our system provides minimal-resistance ion transport paths in the electrolyte phase, enabling specimens with thickness of at least $\sim$500 µm, which is 30-50 times thicker than literature values for comparable systems$^{20,108,119}$.
On a volumetric basis, accounting for the total volume of the half-cell (including the electrolyte in the pores), our electrodes show exceptional and highly tunable performance, as presented in Figure 55b. First and foremost, Figure 55b directly demonstrates how the salient electrochemical properties of our composite electrodes can be tuned over a wide range by adjusting the two morphological parameters discussed above, which regulate the amount and spatial configuration of the active material in a given volume. At low power densities, the volumetric energy density of our electrodes ranges from 12.4 to 424 Wh/L as the volume fraction of active material is varied through $S_r$ and $\delta$. Further, our electrodes exhibit power densities up to 219 kW/L at high discharge rates, while still maintaining a large energy density of 97.4 Wh/L. Compared with supercapacitors and full batteries reported in literature, our systems can deliver $20\times$ the energy at high power densities, and $730\times$ the power at comparable energy densities$^{108,119,123}$. Notably, the literature values represent fully assembled cells, and our data is for that of the positive electrode only. Yet our systems demonstrate better performance than both a lithium ion battery and a Ni(OH)$_2$ pseudocapacitor operating at a much wider potential window (2V and 1.8V respectively)$^{108,119}$.

Collectivity, the gravimetric and volumetric Ragone plots in Figure 55 underscore the exceptional performance of our co-continuous composites. To the best of our knowledge, this is the first system that facilely enables direct and independent tuning of the energy and power densities in these materials through morphological adjustments at the length scales relevant to their electrochemical performance. As a result, our electrodes far
outperform the best systems reported in the literature, due to a more efficient spatial arrangement of their various functional phases.

4.1.4. TRANSIENT DIFFUSION MODEL

We postulated that the performance characteristics of our electrodes shown in Figure 55 result from a kinetic competition between the cathode’s electrochemical half-reaction and ion diffusion through the active layer. To test this hypothesis, we present a simple model for transient ion transport in a solid slab. We consider the transient production and diffusion of protons through the electrolytically active material. Since $\xi \gg L$ (note $\xi$ is proportional to the radius of curvature in spinodal structures), we neglect curvature (see Figure 56).

Recall that the redox reaction:

$$\text{Ni}({\text{OH}})_2 \leftrightarrow \text{NiOOH} + \text{H}^+ + \text{e}^-$$

occurs at a constant rate within the diffusion domain, until all dissociable groups are exhausted. This will be represented by a zeroth order reaction with reaction constant $k$ in the model. We denote the reacting species as OH (dissociable groups in Ni(OH)$_2$) and the
diffusing products (protons) as H. Assuming that the Ni phase is impermeable to protons, proton incorporation into the electrolyte occurs much more rapidly than proton diffusion through the solid phase, and the initial concentration of the dissociable groups is $C_0$, the governing equations and boundary and initial conditions are:

$$
\frac{\partial C_H}{\partial t} = D_H \frac{\partial^2 C_H}{\partial x^2} + k
$$

$$
\frac{\partial C_{OH}}{\partial t} = -k
$$

BCs:

$$
\begin{align*}
\frac{\partial C_H}{\partial x} (x=0,t) &= 0 \\
C_H (x=L,t) &= 0
\end{align*}
$$

ICs: $C_H (x,t=0) = 0$, $C_{OH} (x,t=0) = C_0$.

The second equation readily gives: $C_{OH} = C_0 - kt$. This in turn allows us to find the total duration of the experiment, $t_r$, which is the time needed for all dissociable groups to be exhausted (equivalent to the duration that a constant current can be drawn from the system). We get:

$$
t_r = \frac{C_0}{k}
$$

The first differential equation can now be solved for the duration $0 < t < t_r$ using Finite Fourier Transform (FFT). The basis functions and eigenvalues are identified as:
\[ \phi_n(x) = \frac{\sqrt{2}}{L} \cos(\lambda_n x) \quad \lambda_n = \left( n + \frac{1}{2} \right) \frac{\pi}{L}, \quad n = 0, 1, 2, \ldots \]

And the solution through FFT is:

\[ C_{H}(x,t) = \frac{2k}{L D_{H}} \sum_{n=0}^{\infty} \frac{(-1)^n}{\lambda_n^3} \cos(\lambda_n x) \left[ 1 - \exp\left(-\lambda_n^2 D_{H} t\right) \right] \quad 0 < x < L, \quad 0 < t < t_r \]

To proceed, we consider the electrochemical energy density to be proportional to the amount of protons that diffuse into the electrolyte (equivalent to the amount of dissociable groups that are successfully utilized) during the experiment. This can be calculated from the instantaneous proton flux at \( x = L \):

\[ N_{H}(x = L, t) = -D_{H} \frac{\partial C_{H}(x = L, t)}{\partial x} = \frac{2k}{L} \sum_{n=0}^{\infty} \frac{(-1)^{2n}}{\lambda_n^2} \left[ 1 - \exp\left(-\lambda_n^2 D_{H} t\right) \right] \]

The total amount of protons that diffuse into the electrolyte per unit active material/electrolyte interfacial area is then:

\[ G = \int_{0}^{t_r} N_A(x = L, t) \ dt = \frac{2k}{L} \sum_{n=0}^{\infty} \frac{(-1)^{2n}}{\lambda_n^2} \left[ t_r + \frac{1}{D_{H} \lambda_n^2} \left( \exp\left(-\lambda_n^2 D_{H} t_r\right) - 1 \right) \right] \]
To convert this expression to one of Energy Density \( (E) \) as a function of Power Density \( (P) \), we use:

\[
t_r = \frac{C_0}{k}, \quad k = \frac{2\rho P}{nF\Delta V}, \quad E = \frac{nF\Delta G}{2L\rho},
\]

where \( n \) is the stoichiometric number of electrons involved in the reaction, \( F \) is Faraday’s constant, \( \Delta V \) is the applied voltage, and \( \rho \) is the density of nickel hydroxide. Therefore, \( E \) and \( P \) are related as:

\[
E = \frac{nF\Delta V}{3.6L^2\rho} \sum_{\omega_0} \left[ \frac{C_0}{\lambda_i^2} + \frac{2\rho P}{nF\Delta V D_H \lambda_i^4} \left( \exp \left( -\frac{\lambda_i^2 D_H C_0 nF\Delta V}{2\rho P} \right) - 1 \right) \right]
\]

where a factor of 3.6 \text{ W.s.g}^{-1}/\text{W.h.kg}^{-1} is also introduced for unit conversion.
FIGURE 57. MODEL PREDICTIONS. (A) DATA FOR THE 15/1000 ELECTRODE FROM FIGURE 55A COMPARED WITH THE MODEL PREDICTIONS. (B) EXTRACTED $a_3$ VALUES VERSUS ACTIVE MATERIAL THICKNESS COMPARED TO THE EXPECTED $L^{-2}$ DEPENDENCY.

To test the applicability of our model, we focus on the dominant ($i = 0$) terms in the series, for which the solution takes the form:

$$E = a_1 + a_2 P \left( \exp \left( -\frac{a_3}{P} \right) - 1 \right)$$

EQUATION 7. MODEL OF THE ENERGY AND POWER DENSITY OF THE COMPOSITE ELECTRODES.

with $a_1 = \frac{nF\Delta V C_\theta}{3.6L^2 \rho \lambda_0^3}$, $a_2 = \frac{1}{1.8L^2 D_H \lambda_0^4}$, and $a_3 = \frac{\lambda_0^2 D_H C_\theta nF\Delta V}{2\rho}$. Therefore, a three-parameter fit based on Equation 7 to the data in Figure 55a would test the validity of the above model. It must be noted that the model parameters are not all freely adjustable: here the only unknowns are $C_\theta$ and $D_H$, for which theoretically expected values (or ranges) are available. As a representative example, Figure 57a shows the data for the 15/1000 electrode from Figure 55a, together with a three-parameter fit based on Equation 7.
Excellent agreement between the data and the model is observed, with $a_1 = 184.2$ Wh/g, $a_2 = 4.4545$ s, and $a_3 = 60.486$ kW/kg. A similar level of agreement is also achieved for the other specimens, as shown in Figure 58. From the collective values of the model parameters extracted from all experiments (as shown in Table 2), we calculate $C_0 = 0.0766 \pm 0.0092$ mol OH$^-$/cm$^3$ and $D_H = 3.55 \times 10^{-9} \pm 1.55 \times 10^{-9}$ cm$^2$/s, which are consistent with the theoretically expected $C_0 = 0.0885$ mol OH$^-$/cm$^3$ and $6.4 \times 10^{-11}$ cm$^2$/s < $D_H < 3.4 \times 10^{-8}$ cm$^2$/s (ref 129).

---

**FIGURE 58. MODEL PREDICTIONS.** DATA FOR ALL REMAINING ELECTRODES FROM THE GRAVIMETRIC RAGONE PLOTS COMPARED TO MODEL PREDICTIONS.
Our model also predicts that the critical power density, $P_c$, which is the value at which transport limitations begin to affect the electrode’s performance, must scale with the active layer thickness as $P_c \sim nF\Delta V C_0 D_0 / 2\rho L^2$. From Equation 7, this occurs when $P$ becomes comparable to $a_3$. Therefore, to further test the validity of our model, in Figure 57b we compare the extracted values of $a_3$ for all electrodes with the predicted $1/L^2$ scaling. Again, our experimental observations are fully consistent with the predictions of our transient diffusion model. This analysis provides a mechanistic understanding of the electrode’s performance as a kinetic competition between the redox reaction and ion transport within the active layer. In this context, any microstructural changes during charge/discharge will likely be manifested through variations in the diffusion coefficient. The superior performance of our electrodes thus stems from our ability to simultaneously maintain a short ion diffusion path through the solid phase, a large volume fraction of the active material, high ion supply rates through the uniform electrolyte channels, and co-continuity of all phases. These characteristics, uniquely afforded by the particular morphology of our bijel-based composites, provide straightforward and rapid access to the entirety of the active material during the electrode’s operation.

<table>
<thead>
<tr>
<th>ELECTRODE</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/675</td>
<td>151.3</td>
<td>0.856</td>
<td>4012</td>
<td>0.964</td>
</tr>
<tr>
<td>8/1000</td>
<td>176.8</td>
<td>4.956</td>
<td>46.20</td>
<td>0.987</td>
</tr>
<tr>
<td>15/475</td>
<td>123.9</td>
<td>0.339</td>
<td>12143</td>
<td>0.776</td>
</tr>
<tr>
<td>15/675</td>
<td>167.5</td>
<td>1.119</td>
<td>4180.8</td>
<td>0.987</td>
</tr>
<tr>
<td>15/1000</td>
<td>184.2</td>
<td>4.455</td>
<td>60.486</td>
<td>0.993</td>
</tr>
<tr>
<td>22/675</td>
<td>150.3</td>
<td>0.998</td>
<td>3805</td>
<td>0.908</td>
</tr>
<tr>
<td>22/1000</td>
<td>177.3</td>
<td>3.663</td>
<td>72.669</td>
<td>0.966</td>
</tr>
</tbody>
</table>

TABLE 2. EXTRACTED $a_1$, $a_2$, $a_3$ AND $R^2$ VALUES FROM THE MODEL PREDICTIONS FOR EACH ELECTRODE.
4.1.5. SUMMARY

In conclusion, we have synthesized three-dimensional, co-continuous Ni/Ni(OH)$_2$ porous electrodes derived from bijels which offer robust tuning of the energy and power densities, resulting in a 730× enhancement in power density and a 20× improvement in energy density over comparable systems previously reported in the literature. Further, our fabrication technique allows for electrodes that are significantly thicker than previously reported systems, enabling larger amounts of total stored energy. This level of performance is due to the unique microstructure of these bijel-derived composites, which are comprised of uniform, co-continuous phases whose characteristic length scales can be tuned independent of one another. As such, electrodes can be designed to meet a variety of different performance characteristics. The synthesis strategy introduced here can be expanded beyond Ni/Ni(OH)$_2$ chemistries, offering a robust platform for the fabrication of microstructured composites for the next generation of electrochemical devices and energy materials.

4.2. CARBON/SILICON ELECTRODES

Lithium-ion batteries (LIBs) have emerged in the past decade as the most promising battery technology because they offer high energy density (second only to metal-air batteries), high operating voltage, long cycle life and low self-discharge. However, the performance of the cell is greatly hindered by the achievable energy density of the anode. Commercialized batteries rely on graphitic anodes, which have a relatively low specific lithiation capacity of 372 mAh g$^{-1}$ (LiC$_6$)$^{131}$. Nonetheless, carbon based materials have been the most widely used and studied anode materials for LIBs due to their low cost and the
ability to reversibly intercalate lithium into the carbon host lattice, leading to good cyclability and safety. To increase the performance of carbon-based anodes, researchers have looked at turbostratic, amorphous and nanostructured carbons as well as graphene based anodes\textsuperscript{132-138}. While each of these attempts surpassed the theoretical specific capacity of carbon, the values achieved for specific capacity were still relatively low. To further advanced LIBs performance, new materials besides carbon must be considered. In particular, other metallic and semi-metallic materials offer specific capacity values much higher than carbonaceous material, and can be electrochemically alloyed with lithium\textsuperscript{139}. Of these materials, silicon offers the highest specific capacity, with a theoretical value of 4212 mAh/g (corresponding to Li\textsubscript{22}Si\textsubscript{5}, which is the highest lithium containing alloy phase in the Li-Si system), over ten times that of graphite\textsuperscript{140}. However, the main drawback in the use of silicon is the large volume change that occurs during the Li alloying and dealloying process\textsuperscript{141}. For silicon, this volume change is \~300\% and can lead to high stress points and severe cracking, leading to loss of electrical contact in the material which causes a sizeable irreversible capacity, leading to a poor cycle life\textsuperscript{142}. To combat this, there has been a push towards nano-architectured electrodes, which has been shown to both improve the overall specific capacity as well as the cycle lifetime\textsuperscript{140,143,144}. Additionally, due to the low conductivity of silicon, it has been shown necessary to have a current collector (normally carbon), for transport of electrons throughout the electrode\textsuperscript{144}. Thus, this work aims to synthesize a 3D carbon/silicon electrode derived from bijels to be used as an anode for LIBs. The unique microstructure of a bijel, due to its node-less structure, could possibility withstand the large volume expansion and contraction of silicon without creating local stress points that can significantly hinder its electrochemical performance.
4.2.1. MATERIAL AND METHODS

4.2.1.1. Silica Synthesis

Fluorescents silica colloids with an average diameter of \( <d> = 675 \) nm and a coefficient of variation \( CV = 2.9\% \) were used in this work. Particles were synthesized following the Stöber method\(^{68,70} \). First, dye was prepared by addition of 12.5 mg of rhodamine B isothiocyanate dye to a mixture containing 51.6 µL of (3-aminopropyl)triethoxysilane and 10 mL of anhydrous ethanol and stirred overnight. Particles were then synthesized by the addition of 10 mL of ammonia, 5 mL of the dye solution and 4.18 mL of tetraethylorthosilicate to 35 mL of anhydrous ethanol, and the reaction was allowed to proceed overnight. The particles were then washed in deionized water by repeated centrifugation, dried for 4 hours in an oven at 70°C, and then transferred to a vacuum oven sustained at 110 °C and allowed to dry for several days to achieve near-neutral wetting properties.

4.2.1.2. Formation of W/L Bijels

Bijels were prepared by dispersing the silica particles in Millipore water using an ultrasonic probe at a power of 40 W for 4 minutes, and allowed to cool to room temperature. The water/silica mixture was then combined with a critical amount of 2,6-lutidine (\( x_L = 0.064 \)) and 200 µL of this mixture was added to a homemade microscopy vial (i.d. = 5 mm). Bijels were then formed through ramping the samples into the unstable region in a microwave at a power of 95 W for 30 seconds. The bijels samples were then quickly transferred to an oven maintained at 70°C. After 30 minutes, 50 µL of dipentaerythritol pentaacrylate monomer mixed with a photoinitiator was carefully added to the top of the sample and allowed to diffuse into the lutidine-rich phase. After 4 hours,
the monomer-rich phase was polymerized by an ultraviolet lamp, and the remaining fluid domain was drained, producing a bicontinuous polymer scaffold.

4.2.1.3. **Synthesis of the C/Si Composite Electrode**

**Carbon Monolith**

The polymer scaffold was transformed to an amorphous carbon monolith by soaking the scaffold in a mixture containing oxalic acid and furfuryl alcohol (molar ratio of alcohol to acid 250:1). After 30 minutes, the polymer scaffold was removed and allowed to quickly drain the micropores. The sample was transferred to an oven maintained at 100°C and kept there overnight to polymerize the furfuryl alcohol. To remove the polymer and complete the polymerization process of furfuryl alcohol, the sample was sintered at 300°C for 4 hours, 500°C for 4 hours, and 800°C for 2 hours, creating a bicontinuous amorphous carbon monolith.

**Silica to Silicon Transformation**

The silica that remained on the carbon sample was transformed to silicon through a magnesium reduction reaction. Excess magnesium (molar ration \( \text{Mg:SiO}_2 > 10:1 \)), along with the carbon/silica sample was added to Swagelok reaction vessel in a controlled environment (under argon). The reaction vessel was heated to 675°C under the flow of Ar, and left to react for 30 minutes. The sample was then removed from the reaction vessel, and heated to 675°C for one hour and 5 minutes under the flow of Ar to complete the reaction. MgO was then etched from the sample with concentrated HCl overnight. Any remaining silica was etched 14.45M HF, creating the final C/Si composite electrode.
4.2.1.4. Characterization

Scanning electron microscopy was performed using a FEI Magellan 400 XHR. All X-Ray Diffraction experiments were conducted using a Rigaku SmartLab. All materials were weighed using a Radwag MYA 2.3Y microbalance with 1 mg readability. Thermogravimetric analysis was performed on a TA Q500.

4.2.2. INITIAL RESULTS

Silica can easily undergo a magnesium reduction reaction to create pure silicon\textsuperscript{145,146}. The reaction mechanism is as follows:

\[ 2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + Si(s), \]

where magnesium vapor reduces silica through oxidation of magnesium. Since the colloidal particles used to stabilize bijels are silica particles, this creates a somewhat simple and straightforward pathway to create highly porous, three-dimensional composite silicon electrodes. The thermodynamics of this reaction can be easily understood by analyzing an Ellingham diagram. These diagrams plot the change in Gibbs free energy ($\Delta G$) for the oxidation reactions of various metals as a function of temperature. In order to compare the various reactions, the values for $\Delta G$ consider the same quantity of oxygen (in this case 1 mole of $O_2$). Of importance for this study, a metal (in its reduced form) that has a lower $\Delta G$ at a certain temperature will act as a reducing agent and reduce an oxide with a higher $\Delta G$. Moreover, the wider the gap between the two lines on the graph, the greater effectiveness as a reducing agent. Thus, as can be seen in Figure 59, magnesium (given by the red line) can reduce silica (given by the blue line) over a wide range of temperature values. Also, there are a variety of other metals that could act as a reducing agent for silica. However,
only calcium would have a greater effectiveness than magnesium. Nevertheless, given the higher temperature required to vaporize calcium (Figure 59\textsuperscript{147}), and only the modest gain in reduction potential, it is more desirous to use magnesium as a reducing agent.

**FIGURE 59. ELLINGHAM DIAGRAM HIGHLIGHTING THE CURVES FOR BOTH MG AND SI (REPRODUCED FROM REF. 147).**
The one known issue with this reaction is that not all of the silica is transformed to silicon; typically only ~50% of the silica is transformed\textsuperscript{145,146}. To address this issue, it was recently shown that when this reaction is performed under mild vacuum ($P = 0.1$ Torr), over 98% of the silica can be transformed to pure silicon\textsuperscript{148}. Thus, initial attempts to create a carbon/silicon composite electrode used this approach. To validate this processing technique, tests were first performed on silica particles alone (without the presence of carbon).

Silica particles were added to a reaction vessel containing magnesium in a 2.2:1 molar ratio (Mg:SiO$_2$). Note that this ratio is slightly higher than the required 2:1 molar ratio for the reaction to go to completion. This is due to the fact that a small hole was drilled in the top of the reaction vessel to allow the contents to come to the equilibrium pressure of the furnace during heat treatment, allowing for some magnesium vapor to exit the vessel during the reaction. The reaction vessel used for these experiments is shown in Figure 60. This reaction vessel was sealed under argon, and placed in a tube furnace with...
the pressure adjusted to 3 Torr for the duration of the reaction. The sample was reacted for 45 minutes at 675°C. XRD analysis of the as obtained powder is shown in Figure 61a. The pattern can be indexed to JCPDS card #00-004-0829 (magnesium oxide) and JCPDS card #01-070-5680 (silicon). To remove the MgO, the particles were etched in concentrated HCl overnight, and washed with repeated centrifugation in deionized water until a neutral pH was obtained. XRD analysis of the etched particles is shown in Figure 61b, and the pattern can be indexed to JCPDS card # 01-070-5680 (silicon). The final product is pure silicon, with some remaining amorphous silica (shown by the slight amorphous peak in both XRD patterns in Figure 61.

Since this reaction process was verified for silica particles, this same approach was taken for carbon monoliths decorated by silica particles. First, amorphous carbon monoliths were created as outlined in Section 4.2.1.3, and the resulting morphology is shown in Figure 62. The sample clearly has the overall microstructure of a bijel, with silica particles coating the carbon domains. In order to determine the mass of SiO₂ in the
samples, thermogravimetric analysis experiments were performed on a portion of the same sample, before the reaction was allowed to proceed. These tests measure the carbon content (through the amount of carbon burned off during the test) of the samples, allowing for determination of the silica content in each sample. TGA curves of various samples are shown in Figure 63, and as can be determined from these curves, the actual amount of silica in these samples can vary drastically between samples, thus TGA should be performed on each individual sample.

**FIGURE 62.** SEM IMAGE OF THE CARBON/SILICA MONOLITH. THE OVERAL MORPHOLOGY IS THAT OF A BIJEL, AND THE INSET SHOWS THAT SILICA PARTICLES COVER THE CARBON DOMAINS. THE SCALE BAR FOR THE LARGE IMAGE IS 100 µM AND IS 10 µM FOR THE INSET.
As mentioned above, initial tests were performed under the same conditions as the silica particles (45 minutes at 675°C at a pressure of 3 torr.). However, it was determined that there was enough oxygen in the surrounding environment to oxide the carbon (which acts as both the current collector in this composite electrode as well as the mechanical backbone). To rectify this, additional tests were performed under the flow of argon, at atmosphere pressure. Due to the presence of carbon (and atmospheric pressure conditions), it was determined that a reaction time of at least 5 days was needed to convert at least some of the silica to silicon. Even with this lengthily reaction period, only a small percentage (~4%) of the silica is converted. Thus, in order to fully convert or at least convert an appreciable amount of the silica, very long reaction times are necessary.
Consequently, in order to make this process more feasible, additional reaction conditions were explored.

As mentioned briefly above, magnesium reduction of silica is typically performed at a 2:1 molar ratio (Mg:SiO₂) to ensure that no undesired phases are created (i.e. Mg₂Si). This also guarantees that the initial silica microstructure is maintained, due to the high melting point of Si (1414°C, well above the reaction temperature of 675°C)¹⁴⁵,¹⁴⁹. However, if retention of the original shape of the silica is not of importance, then the original undesirous phase of Mg₂Si is no longer a concern¹⁵⁰, because magnesium silicide can decompose into MgO and Si, leaving pure Si once the oxide phase is etched in HCl¹⁵¹. The reaction mechanism for the initial formation of Mg₂Si can follow one of two proposed routes. In the first route, the Mg vapor first reacts with the silica to form magnesium oxide and silicon, and if Mg is continuously supplied, it will react with the formed Si to produce magnesium silicide¹⁵²,¹⁵³:

\[
SiO_2(s) + 2Mg(g) \rightarrow Si(s) + 2MgO(s) \Delta G = -245.2 \text{ kJ/mol}
\]

\[
Si(s) + 2Mg(g) \rightarrow Mg_2Si(s) \Delta G = -63.4 \text{ kJ/mol}
\]

More recently, it was proposed that magnesium silicide can be formed directly (when the reaction occurs under mild vacuum) via the following reaction¹⁴⁸:

\[
SiO_2(s) + 4Mg(g) \rightarrow 2MgO(s) + Mg_2Si(s) \Delta G = -308. \text{ kJ/mol}
\]

In this work, the reaction occurs under atmospheric pressure, but also with a rich supply of Mg (much larger molar ratio than previous studies). Thus, additional experiments coupled
with XRD analysis need to be performed to analyze which reaction scheme (or both) applies to our samples. Nonetheless, magnesium silicide and magnesium oxide are the final products at this stage of the reaction. To then transform the Mg$_2$Si to Si, oxygen is required (either in the from of O$_2$ or SiO$_2$). This process then process via one (or both) of the following mechanisms:

\[
Mg_2Si(s) + SiO_2(s) \rightarrow 2Si(s) + 2MgO(s)
\]

\[
Mg_2Si(s) + O_2(g) \rightarrow Si + 2MgO
\]

Most likely, a mixture of these two processes will occur, unless all the silica was consumed in the initial reaction.

Samples were tested following the above reaction mechanism. Briefly, the carbon/silica sample along with excess Mg (molar ratio of Mg:SiO$_2$ > 10:1), was added to a Swagelok reaction vessel under inert conditions. The samples were heated to 675°C for 30 minutes to transform the silica to magnesium silicide and magnesium oxide. XRD patterns of the samples at this state are shown in Figure 64, and can be indexed to JCPDS card #00-004-0829 (magnesium oxide) and JCPDS card #00-034-0458 (magnesium silicide). The samples were then reacted at 675°C for one hour and 5 minutes under Ar, without any magnesium present. While this reaction is done under Ar, it is believed that the inert gas has a small percentage of O$_2$ present (even though ultrapure Ar was used), due the weight gain (~14.6%) of the sample during this process. This small amount of oxygen is crucial for the reaction to proceed (see above reaction mechanism), but is also low enough as to not oxide and thus remove the carbon backbone. Figure 64b displays the XRD pattern of the
FIGURE 64. XRD PATTERNS FOR THE SAMPLE AFTER A) 30 MINUTES WITH EXCESS Mg, B) AN HOUR AND 5 MINUTES UNDER Ar (NO Mg PRESENT) AND C) THE FINAL CARBON/SILICON ELECTRODE.
sample after this reaction step, and be indexed to JCPDS card #00-004-0829 (magnesium oxide) and to JCPDS card # 01-070-5680 (silicon). Thus, all of the Mg₂Si was transformed to MgO and Si during this process. The MgO was etched from the sample using HCl, and the resulting electrode contained silicon and amorphous carbon (Figure 64c, indexed to JCPDS card # 01-070-5680 silicon). However, a very broad, small peak is also present at 2θ = 35°, which can be indexed to silicon carbide (SiC). Recently, it has been shown that SiC can form at relatively low temperatures (600°C) through the magnesiothermic reduction reaction when excess Mg is present.\textsuperscript{154-157} While the overall reaction mechanism is still not completely understood, the following reaction mechanism is proposed:

\[ 2Mg + SiO_2 \rightarrow 2MgO + Si \]

\[ Si + C \rightarrow SiC. \]

The first step of the process is the same as our reaction mechanism, and the second step utilizes Mg as a catalyst in order for the reaction to proceed at such low temperatures. Since our material has an abundance of Mg as well as carbon, some SiC could be formed during our synthesis approach. Further timed studies need to be preformed in order to determine if this unwanted side product could be bypassed during synthesis. Nonetheless, our resulting sample is an amorphous carbon monolith decorated with silicon, as shown in Figure 65. Moreover, while some of the original silica particles retained their shape during the transformation to silicon (inset of Figure 65), most of the silicon takes the shape of nanoporous domains (similar to the overall morphology of bijels). This can be understood through the two reaction mechanisms for the formation of Mg₂Si explained earlier. In the
first reaction mechanism, silica is first reduced to silicon, and the excess magnesium reacts with the newly formed silicon to produce magnesium silicide. In the initial formation of silicon, the original shape of the silica is maintained\textsuperscript{145,149}. Thus, if not all of the newly formed silicon reacts with the excess magnesium, you would expect to have some silicon maintain the original shape of the silica particles. As mentioned above, when magnesium silicide is produced, it will greatly distort the original shape of the silica\textsuperscript{150}. The nanoporous domain shown in Figure 65 is mostly likely the result of dealloying of Mg\textsubscript{2}Si during the second reaction step to form pure silicon. Nonetheless, the resulting structure provides a hierarchical structure with small silicon domains (\textasciitilde 60nm) and large domains (\textasciitilde 30 \textmu m) for the electrolyte to free flow throughout the structure.
4.2.3. SUMMARY AND FUTURE WORK

This section outlined the synthesis approach for a hierarchically porous carbon/silicon electrode to be used as an anode for lithium ion batteries. Through a simple chemical processing technique, the bijels can be easily converted to carbon monoliths. Uniquely in this synthesis procedure, the silica particles used to arrest the bijel structure are no longer disregarded, but instead are an integral part to the final composite electrode. Through a magnesiothermic reduction of the silica, it is transformed to nanoporous silicon that decorates the carbon monolith. The approach laid out in this section provides a unique
method to create carbon/silicon anodes with a distinctive co-continuous morphology. Future work should focus on fine-tuning this synthesis procedure in order to ensure that all the silica is converted to silicon. Once the overall synthesis technique is finalized, it should be electrochemically characterized through charge/discharge tests as well as cyclic voltammetry, to determine how the morphology impacts the overall performance of the electrode.
5. SUMMARY AND FUTURE WORK

5.1. SUMMARY

This dissertation uses a relatively new soft material, a bicontinuous interfacially jammed emulsion gel (bijel), as a template to create co-continuous composite electrodes that can help bridge the gap between supercapacitors and batteries. In Chapter 2, this soft material was introduced along with the manner in which it can be processed into a polymer template to create an array of materials. The processability of bijels was linked to its rheological properties and it was determined that the bijel must be able to withstand Marangoni stresses along the fluid interface that can occur when monomer is introduced to the system (causing a gradient of the liquid interfacial tension). In Chapter 3, a new bijel system we termed bridged bijel (in which one of the fluid domains contains bridged droplets), was introduced and the rheological properties of this soft material as well as simple bijels were explored in more detail. In particular, an exponential relationship between particle volume fraction and $G'$ was experimentally determined. Additionally, the relationship between domain size and particle volume fraction was explored for this bijel system. Due to the mechanical stability that the bridged droplet network provides, bridged bijels can access domains up to 4x that of simple bijels, providing a robust way to access exceedingly large domains. Chapter 4 outlines the synthesis approach to create two different composite electrodes, Ni/Ni(OH)$_2$ and C/Si, to be used a positive and negative (respectively) electrode for energy storage systems. An array of electrodes with the Ni/Ni(OH)$_2$ chemistry was synthesized, showing the versatility in the process technique which allows for independent tuning of domain size (indirectly changing the volumetric...
density of the active material) as well as the thickness of the active material, which directly controls the obtained power density. Through this route, composite electrodes were created with the energy density of batteries and the power density of supercapacitors, bridging the gap between these two technologies. Additionally, the fabrication approach can be applied to a myriad of materials, creating a robust platform to make highly porous, co-continuous composite electrodes.

5.2. FUTURE WORK

This dissertation outlines the first successful application of bijels, in particular as composite electrodes for high energy and power energy storage systems. However, this is just one of the many possible applications for this unique material, as co-continuous morphologies are ideal for a multitude of applications, from tissue engineering, separations and sensors to name a few. Additionally, there is still much fundamental knowledge to be gained from the study of this soft material. First, as mentioned in Section 2.1.5, I explored a few other fluid systems that undergo spinodal decomposition and was able to arrest these systems with colloidal silica to create bijels. These systems, and other fluids systems that undergo spinodal decomposition, should be explored in greater detail. In particular, with the two new fluid systems mentioned in this work, a new processing technique that could greatly expand upon the current set of monomers can be utilized. Through these systems, it is possible to fully freeze or solidify one of the fluid domains. This processing method does not require for the monomer to selectively partition into one of the fluid domains, thus allowing for the ability to use any monomer that can be UV cured.
Currently only silica particles have been used to stabilize bijels, however conductive particles such as carbon, nickel or gold could be used to create conductive bijels. Through simulations it has been proposed that bijels stabilized with magnetic particles could offer a manner for controlled breakdown of the structure, as well an approach to control the shape of the fluid domains\textsuperscript{158}. A recent study used rod shaped silica particles to stabilize the NM/EG system\textsuperscript{66}, and additional particles shapes (such as cubes) could be explored as well as the effect of particle size on the domain size and processability.

While this work introduced two different composite electrode chemistries, there are countless materials that can be used for energy storage that could be explored for these applications. Additionally, full batteries, consisting of an anode and a cathode with bijel morphologies could be synthesized and tested. Moreover, the morphology of a bijel could be ideal for the creation of a full 3D battery (Figure 66). Through integration of thin layers of an anode, solid electrolyte and cathode on the basic structure of the bijel, a full 3D battery could be constructed that offers short transport lengths for ions and electrons throughout the volume, as well as increased volumetric capacity.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig66}
\caption{FIGURE 66. SCHEMATIC FOR THE DESIGN OF A FULL 3D BATTERY DERIVED FROM BIJELS.}
\end{figure}
6. APPENDIX

6.1. ADDITIONAL ELECTROCHEMICAL TESTS FROM SECTION 4.1.3

**FIGURE 67.** ELECTROCHEMICAL MEASUREMENTS OF THE 8/675 Ni/Ni(OH)₂ COMPOSITE ELECTRODE. (A) CV CURVES AT VARIOUS SCAN RATES; (B) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF SCAN RATE; (C) GALVANOSTATIC DISCHARGE CURVES AT VARIOUS CURRENT DENSITIES; (D) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF CURRENT DENSITY.
Figure 68. Electrochemical measurements of the 8/1000 Ni/Ni(OH)$_2$ composite electrode. (A) CV curves at various scan rates; (B) gravimetric specific capacitance values as a function of scan rate; (C) galvanostatic discharge curves at various current densities; (D) gravimetric specific capacitance values as a function of current density.
FIGURE 69. ELECTROCHEMICAL MEASUREMENTS OF THE 15/475 Ni/Ni(OH)₂ COMPOSITE ELECTRODE. (A) CV CURVES AT VARIOUS SCAN RATES; (B) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF SCAN RATE; (C) GALVANOSTATIC DISCHARGE CURVES AT VARIOUS CURRENT DENSITIES; (D) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF CURRENT DENSITY.
FIGURE 70. ELECTROCHEMICAL MEASUREMENTS OF THE 15/675 Ni/Ni(OH)₂ COMPOSITE ELECTRODE. (A) CV CURVES AT VARIOUS SCAN RATES; (B) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF SCAN RATE; (C) GALVANOSTATIC DISCHARGE CURVES AT VARIOUS CURRENT DENSITIES; (D)
GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF CURRENT DENSITY.

FIGURE 71. ELECTROCHEMICAL MEASUREMENTS OF THE 15/1000 Ni/Ni(OH)\textsubscript{2} COMPOSITE ELECTRODE. (A) CV CURVES AT VARIOUS SCAN RATES; (B) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF SCAN RATE; (C) GALVANOSTATIC DISCHARGE CURVES AT VARIOUS CURRENT DENSITIES; (D) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF CURRENT DENSITY.
FIGURE 72. ELECTROCHEMICAL MEASUREMENTS OF THE 22/1000 Ni/Ni(OH)$_2$ COMPOSITE ELECTRODE. 
(A) CV CURVES AT VARIOUS SCAN RATES; (B) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF SCAN RATE; (C) GALVANOSTATIC DISCHARGE CURVES AT VARIOUS CURRENT DENSITIES; 
(D) GRAVIMETRIC SPECIFIC CAPACITANCE VALUES AS A FUNCTION OF CURRENT DENSITY.
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