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THE Li/Li₃N ELECTRODE:
STUDY OF ITS ELECTROCHEMICAL BEHAVIOR IN AN
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ABSTRACT

Lithium nitride has been studied as a possible solid-electrolyte interphase between the lithium electrode and an organic electrolyte. The Li/Li$_3$N electrode has been obtained by exposing lithium to a pure nitrogen atmosphere at ambient temperature. This formation is found to result in a porous lithium nitride film, associated with a decrease in the molar volume during the reaction. The impedance behavior of the Li/Li$_3$N electrode can be interpreted by a porous-film model deduced from a transmission-line model. The slow filling of the micropores of the film and reaction of the lithium with electrolyte at the pore bottom are responsible for changes of impedance and open circuit potential with time and under cycling.
1. INTRODUCTION

When a lithium electrode is stored in an organic electrolyte, a surface layer is usually formed, due to the decomposition products of the solvent in the presence of lithium [1]. This surface layer inhibits the successful cycling of the lithium electrode. One way to limit the formation of this surface layer is to create an interphase that is less reactive than lithium between the electrode and the electrolyte.

A survey of the literature suggests that lithium nitride may be an excellent candidate for this purpose: it is a solid electrolyte with good ionic conductivity [2]. The use of lithium nitride as a protective film against the chemical corrosion of lithium in organic electrolytes has been proposed by Muller and Schwager [3]. In their experiments, lithium nitride was prepared at room temperature by exposing lithium under pure and diluted nitrogen. A study of impedance data during the immersion of the lithium/lithium nitride electrode demonstrated that the presence of lithium nitride reduced the formation rate of the surface layer in propylene carbonate-based electrolytes.

The purpose of this report is to analyze the electrochemical behavior of the lithium electrode covered by a lithium nitride film formed at ambient temperature. The study was carried out by electrode-impedance spectroscopy. The organic electrolyte was a solution of lithium perchlorate in propylene carbonate.
2. LITERATURE REVIEW

An extensive review of the properties of lithium nitride has been presented recently by Rabenau [2]. The following summary is devoted only to understanding its crystal structure and conduction mechanism.

2.1 Crystal Structure of Lithium Nitride

Lithium nitride, \( \text{Li}_3\text{N} \), has a characteristic two-dimensional structure based on a hexagonal lattice. It has a highly symmetric structure (space group \( \text{P6/mmm} \)) in which the nitrogen ions are surrounded by 8 lithium atoms, 6 in one plane, with one underneath and one above, as illustrated in Fig. 2-1. In other words, this structure contains tightly bonded \( \text{Li}_2\text{N} \) layers with the nitrogen in the center of hexagonal lithium arrays. These layers are connected by the remaining 1/3 of the lithium ions, which bridge the nitrogen ions of adjacent layers. This arrangement was first proposed by Zintl and Brauer [4] and was recently confirmed by Rabenau and Schultz [5]. It can be shown that only the \( \text{Li}(2) \) ions in the \( \text{Li}_2\text{N} \) layers can move, while the \( \text{Li}(1) \) ions are relatively immobile. Among the \( \text{Li}(2) \) positions, 1-2% are not occupied, whereas the \( \text{Li}(1) \) positions are fully occupied. Thus the empty \( \text{Li}(2) \) positions provide a mechanism for the motion of the \( \text{Li}(2) \) ions in the \( \text{Li}_2\text{N} \) layers.
2.2 Ionic Conductivity in Li$_3$N Single Crystals

The basic study on ion conductivity in Li$_3$N single crystals has been carried out by Von Alpen, Rabenau, and Talat [6]. The lithium nitride single crystals they studied were obtained by the Czochralski method, in which a small oriented seed crystal is dipped into the melt and pulled out slowly while being rotated.

The study of ionic conductivity $\sigma$ by electrode-impedance spectroscopy allows one to verify the anisotropic properties of the Li$_3$N single crystals due to their bidimensional structure. The main results are shown in Fig. 2-2a, a plot of logarithm $\sigma T$ versus the reciprocal of the absolute temperature. It was found that $\sigma_{//}$, the conductivity parallel to the crystallographic layers, is orders of magnitude greater than $\sigma_\perp$, the conductivity perpendicular to the layers.

2.3 Ionic Conductivity in Li$_3$N Sinters

The basic study of ionic conductivity in Li$_3$N sinters has been carried out by Boukamp and Huggins [7]. Lithium nitride was formed by reacting molten lithium with nitrogen in a crucible at 180°C. The product was crushed and milled. The Li$_3$N powder was pressed and then sintered in purified nitrogen between 650 and 750°C.

The lithium nitride sinters had two types of conductivity, which were detected by electrode-impedance spectroscopy. The first type was the transcrystalline conductivity $\sigma_t$, which corresponds to
the average conductivity inside each grain of the polycrystalline sample. The second type was the intercrystalline conductivity \( \sigma_i \), related to the intergranular structure of the sintered sample. The main results, shown in Fig. 2-2b, are that \( \sigma_t \) is much larger than \( \sigma_i \) over a large temperature range.

3. THEORETICAL

3.1 Models for the Impedance Behavior of the Li/Li\(_3\)N Electrode

The electrochemical behavior of the Li/Li\(_3\)N electrode in an organic electrolyte depends primarily on the morphology of the lithium nitride film. This film, which consists of an anisotropic solid electrolyte, is in the polycrystalline form when it is obtained at room temperature. If no other complications arise, the decrease in the average conductivity in a polycrystal compared to that observed in a single crystal is likely to be related to the amount of space between the particles and by the various orientations adopted by each particle. Thus two main cases can be considered: (1) a relatively compact lithium nitride film formed by many particles with few interparticle voids; (2) a relatively porous lithium nitride film, with many interparticle voids or micropores in contact with the organic electrolyte.
3.2 Model of a Compact Lithium Nitride Film

The impedance behavior of a compact electrode in the presence of an organic electrolyte can be studied more easily when the electrode/film and film/solution interfaces are taken into account.

The film/solution interface is represented by the solution resistance $R_Q$ in series with the Faradaic impedance placed in parallel with the double-layer capacitance. For the case of a pure ionic conductor, for which no charge transfer occurs at the film/solution interface, the Faradaic impedance is infinity. Besides, for the conductor of low capacitance, the effect of the double layer capacitance on the total impedance can be considered as negligible. Accordingly, the impedance of the film/solution interface can be reduced to the solution resistance.

The electrode/film interface is represented by the equivalent circuit of a solid electrolyte on a nonblocking electrode (see Appendix I). For a polycrystalline material, as shown in Fig. 3-1, the transcrystalline and intercrystalline conduction processes are defined by different circuits [7,8]. The resistance $R_t$ associated with the capacitance $C_t$ is related to the conductivity inside each particle, while the resistance $R_i$ and the capacitance $C_i$ are related to the conductivity between two consecutive particles. For a polycrystalline anisotropic material such as lithium nitride, the resulting circuit is a series of $R_t/C_t$ and $R_i/C_i$ circuits. The impedance of each circuit is defined by the Cole-Cole formula, [9] taking into account a pseudo-RC circuit and a depression parameter.
(see Appendix II). The impedance of the solid film is defined as follows:

\[ Z_T(\omega) = \frac{R_t}{1 + (j\omega R_t C_t)(1 - \alpha_t)} + \frac{R_i}{1 + (j\omega R_i C_i)(1 - \alpha_i)}, \]

where \( \alpha_t \) and \( \alpha_i \) are the depression parameters related to the dispersion of the time constants in the transcrystalline and intercrystalline impedances, respectively.

For the compact-film model as shown in Fig. 3-2, the equivalent circuit is constituted by the solution resistance \( R_\Omega \) in series with the circuit of the polycrystalline solid electrolyte. The resulting electrode-impedance diagram in the complex plane consists of two depressed semicircles resulting from the \( R_t/C_t \) and \( R_i/C_i \) couplings with their corresponding depression parameters \( \alpha_t \) and \( \alpha_i \). The transcrystalline impedance is detected only in the very high-frequency range, while the intercrystalline impedance is found in the intermediate- and low-frequency range.

### 3.3 Model of a Porous Lithium Nitride Film

The impedance behavior of a porous electrode can be studied by a transmission-line model, as introduced by De Levie [10]. Recently, Park and MacDonald [11] have developed a general model for a porous electrode of finite thickness in which the impedance of the backing electrode on the pore base is recognized. This model appears suitable for the study of the electrochemical behavior of the
lithium electrode covered by a porous lithium nitride film.

As the usual simplifying assumptions for a transmission-line model, the lithium nitride is assumed to have a homogeneous porous structure with almost straight, parallel, and cylindrical pores with the same pore base and constant composition for the pore wall, as shown in Fig. 3-3. Thus, as shown in Fig. 3-4, the equivalent electrical circuit for a single pore is determined by the properties of the liquid and solid phases. The liquid-phase filling the pores is the organic electrolyte. (The average liquid-phase resistance per unit pore length is \( R_1/L \).) The solid-phase is the lithium nitride film. (The average solid-phase impedance per unit pore length is \( Z_s/L \).) Under these conditions, the impedance behavior of the Li/Li_3N electrode is determined by two additional impedances: (1) the impedance occurring on the pore base \( Z_b \), independent of the pore length, is the impedance of the Li/liquid-electrolyte interface; and (2) the admittance occurring on the pore wall, \( 1/Z_p \), per unit pore length, is the admittance of the Li_3N/liquid-electrolyte interface.

The total impedance \( Z_T \) resulting from \( n \) straight parallel and cylindrical pores defined by the transmission-line model is defined as follows (see Appendix III):

\[
Z_T = \frac{1}{n} \left\{ \left( \frac{Z_s}{Z_s + R_1} \right) + \frac{2\gamma^{1/2}Z_sR_1 + \gamma^{1/2}(Z_s^2 + R_1^2)C + \delta R_1^2S}{L\gamma^{1/2}(Z_s + R_1)(\gamma^{1/2}S + \delta C)} \right\},
\]
where \( \gamma = \left( \frac{Z_s + R_1}{Z_p L^2} \right), \quad \delta = \left( \frac{Z_s + R_1}{Z_b L} \right), \)

and \( C = \cosh (\gamma^{1/2} L), \quad S = \sinh (\gamma^{1/2} L). \)

Simple modifications allow the equation of the total impedance to be extended to a three-dimensional system by taking into account the fraction of the electrode surface covered by the solid electrolyte, and the number \( n \) of micropores per unit surface area (see Appendix IV). For a solid electrolyte characterized by two types of impedances (transcrystalline and intercrystalline), the computer-generated impedance diagram consists of one or two depressed semicircles over the whole frequency range, as shown in Fig. 3-4, according to the assumptions made for the different components of the electrode impedance.

4. EXPERIMENTAL

4.1 The Organic Electrolyte

The electrolyte under study was a molar solution of lithium perchlorate in propylene carbonate with a residual water content of a few ppm. Propylene carbonate (Burdick and Jackson Lab.) was dehydrated on molecular sieves for about two weeks. Lithium perchlorate (Smith Chem. Co.) was dessicated near its melting point.
(240°C) for one day under a vacuum produced by a primary pump. The choice of the electrolyte seemed to have no effect on the study of the electrochemical behavior of the Li/Li$_3$N electrode.

4.2 The Electrolytic Cell

The electrolytic cell, made of polypropylene, had two opposing openings for the electrode holders and an extrusion compartment for the lithium reference electrode, as shown in Fig. 4-1. The counterelectrode was a lithium disc 2 cm in diameter and 0.1 cm thick, which was pressed onto a stainless steel electrode. The working electrode was the cross section of a lithium cylinder 0.2 cm in diameter and 1 cm thick inserted into a polypropylene holder. The reference electrode was the cross section of a lithium cylinder 0.2 cm in diameter extruded near the side of the working electrode.

4.3 The Li/Li$_3$N Electrode

Lithium nitride was prepared by a reaction at room temperature between lithium and nitrogen. Although the other alkali metals are inert to nitrogen, lithium reacts rapidly with this element in an exothermic reaction. The experiment was carried out in a plastic bag filled with a pure nitrogen atmosphere and placed outside the glove box used for the preparation of the organic electrolyte. The Li/Li$_3$N electrode was formed by cutting the cross section of the lithium cylinder with a blade under nitrogen to form a red-black lithium nitride film. Probably because of the diffusion of nitrogen
into the lithium nitride, the reaction is continuous, since no protective film is formed on the lithium electrode. The electrode obtained after a given exposure time was then put into the glove box to be placed in the electrolytic cell.

A morphological study of the lithium nitride film was made with a scanning electron microscope. Its porosity was studied by an automatic scanning porosimeter.

4.4 The Electrode-Impedance Set-Up

Electrode-impedance data were obtained by the Lissajous-figure technique. As shown in Fig. 4-2, the equipment includes an oscillator (Hewlett Packard, Model 3310A), which drives a potentiostat-galvanostat (Princeton Applied Research, Model 173) in the galvanostatic mode. The oscillating current and voltage were measured by a built-in electrometer monitor (Model 178) and current follower (Model 176), or by two external differential preamplifiers (Princeton Applied Research, Model 113). Current versus voltage was displayed on a storage oscilloscope (Tektronix, Model 5111) equipped with differential amplifiers (Tektronix, Model 5A19).

The alternating-current density was about 0.05 mA/cm², which provided a linear response, as required for valid electrode-impedance measurements. The impedance of a dummy cell consisting of a resistance/capacitance circuit was routinely measured and compared with calculated data to ensure that the equipment was in proper working condition for the study of the
electrode impedance in the frequency range of $10^4$ to $10^{-1}$ Hz. The high-frequency limit is determined essentially in order to avoid artifacts caused by the impedance of the lithium reference electrode, while the low-frequency limit is used because of the quick evolution of the impedance of the electrode as a function of the experimental conditions.

5. RESULTS AND DISCUSSION

5.1 Morphological Properties of the Li/Li$_3$N Electrode

5.1.1 Preparation Procedure

The growth at ambient temperature of the lithium nitride film generally began with the formation of an iridescent film on most of the lithium electrodes exposed to a pure nitrogen atmosphere. The film developed essentially on the circumference of the lithium disc, forming a continuous red-black film over the whole surface after an average time of 20 to 30 minutes. Difficulties were encountered in reproducing the growth of this film; the reasons for these difficulties are not well understood. The quality and speed of cutting with the blade seem to be very important to the initial nucleation of lithium nitride on the lithium surface. The same film growth was obtained in an atmosphere of 50% helium and 50% nitrogen, as well as in an atmosphere of 10% nitrogen and 90% helium. The complete transformation of Li into Li$_3$N was obtained after two hours of exposure in a pure nitrogen atmosphere for a
lithium cylinder 1 cm thick and 2 mm in diameter.

5.1.2 Structural Study

Figure 5-1a is a scanning electron micrograph of the lithium nitride surface. It reveals that the ridges on the lithium electrode due to the cutting were reproduced by the lithium nitride film. After 25 min of exposure of lithium in nitrogen, as shown in Fig. 5-1b, the minimum thickness of the lithium nitride film, in the center, was about $10^{-2}$ cm, while the maximum thickness, at the circumference of the disc, was about 0.5 cm.

A study of a thick lithium nitride film formed after one hour did not reveal any direct evidence of its polycrystalline structure but demonstrated that the lithium nitride film is a porous material. As shown in Fig. 5.1c, cracks and holes on the surface were clues that the volume of lithium nitride is lower than the initial volume of lithium. This observation is consistent with the following analysis of the lattices of lithium and lithium nitride by considering the number of lithium ions or atoms per unit volume.

Lithium has a body-centered cubic lattice ($a = 3.509 \text{ Å}$) [12], and the radius of the lithium atom is 1.24 Å. Figure 5-2 shows the two main crystallographic planes, (001) and (110), necessary to determine the number of lithium atoms per unit volume. For example, a parallelepipedic volume of 172.82 $\text{Å}^3$ has 22 atoms ($2 \times 9$ on the faces, and 4 in the center of the cubes), based on four elementary cells. Thus the number of lithium atoms per unit volume is 0.127 per $\text{Å}^3$. 
Lithium nitride has a two-dimensional structure, based on a hexagonal lattice \((a = 3.65 \text{ Å}, c = 3.87 \text{ Å})\) \([5,13]\). The Li(2)-N distance is 2.13 Å, while the Li(1)-N distance is 1.94 Å. Thus the radius of the lithium ion is about 0.7 Å, and the radius of the nitrogen ion is about 1.4 Å. Two main crystallographic planes, (0001) and (1000), are shown in Fig. 5-3. A parallelepipedic volume corresponding to the average composition of lithium nitride (39 lithium ions for 14 nitrogen ions) can be defined within the rectangle formed by the distance along three nitrogen ions \((2 \times 3.65 \text{ Å})\), the distance along four lithium ions on the [0100] axis \((4 \times 2.13 \text{ Å})\), and the height of the elementary hexagonal cell \((c = 3.87 \text{ Å})\). This volume of 240.69 Å\(^3\) contains 39 lithium ions \((2 \times 16\) in the hexagonal planes and 7 between them). Thus the number of lithium ions per unit volume is 0.162 per Å\(^3\).

The greater number of lithium ions per unit volume in lithium nitride (0.162) compared to the number of lithium atoms per unit volume in lithium (0.127) is certainly related to the low value of the radius of the lithium ion (0.7 Å) compared to that of lithium atom (1.24 Å). This fact explains the decrease of material volume after the transformation of lithium into lithium nitride.

5.1.3 Porosimetry Study

The porosimetry study is based on the analysis of the curve showing the cumulative volume of mercury intruded into the pores and interparticle voids of the Li\(_3\)N sample versus the applied pressure.
The study of the intrusion curves for the three samples, as shown in Fig. 5-4, demonstrates that the cumulative pore volume increases almost continuously as a function of pressure. The pressure range used, up to $6 \times 10^4$ PSIA, appeared insufficient to fill all the pores and interparticle voids with mercury. Thus the Li$_3$N layer had a significant percentage of pores of extremely low radii. Besides, the two changes in the curve slope, for pressures between $5 \times 10^3$ and $10^4$ and between $4 \times 10^4$ and $5 \times 10^4$ PSIA, indicated the presence of two main groups of pores of different radii.

The analysis of the pore-size distribution functions, as shown in Figs. 5-5, 5-6, and 5-7, permits one to complete the preceding observations. The differential pore-volume density (Fig. 5-5) has a slight maximum in the 100-200 Å pore-radius range and a sharp one in the pore-radius range below 25 Å. The differential pore-surface and pore-length densities (Figs. 5-6 and 5-7) show that the porosity of the samples is due essentially to the presence of very small pores or interparticle voids.

The procedure used to determine apparent and true densities of the Li$_3$N film is outlined in Table 5-1, which contains data obtained both before and after mercury intrusion. The external volume is evaluated according to the cylindrical geometry of the sample (lines 1 through 3). Its weight is measured (line 4), leading to the evaluation of the apparent density (line 5). The weight of the mercury-filled sample (line 6) permits one to determine the weight
of the intruded mercury (line 7) and consequently its volume (line 8) (13.55 g/cm$^3$ is the density of mercury). The volume of the intruded mercury equals the volume of the pores and interparticle voids in the sample (line 9). Thus the volume of compact material in the sample can be determined (line 10). The weight of the sample (line 4) divided by its volume (line 10) leads to the determination of the true density (line 11). The three samples in Table 5-1 show that the average density values of the porous and compact Li$_3$N layers are 0.97 (apparent density) and 1.22 (true density), respectively. The last result is in good agreement with the value of 1.29 g/cm$^3$ given for the true density of lithium nitride single crystals [5].

The change in the volume of material during the reaction between lithium and nitrogen to form lithium nitride can be studied by using the following values of the weight and density of Li and Li$_3$N:

Li: weight 6.94, density 0.534.

Li$_3$N: weight 34.826, density 1.29.

Three Li equivalent atoms, which have a volume of 39 cm$^3$ can form with nitrogen one equivalent Li$_3$N, with a volume of 27 cm$^3$ for a compact material. These typical values show that the formation of Li$_3$N by exposure to Li in a N$_2$ atmosphere at room temperature leads
to about 30% of decrease of the molar volume. These results confirm that the procedure used for the preparation of Li$_3$N is only adequate for the formation of a porous film.

5.2 Kinetic Properties of the Li/Li$_3$N Electrode

5.2.1 Thermodynamic and Polarization Data

The value of the open-circuit potential $E$ of lithium nitride can be evaluated by means of the value of the standard free energy of formation $\Delta G_0$ of this compound, according to the following equation:

$$\Delta G_0 = -nFE,$$

where $n$ is the number of equivalent mole and $F$ is Faraday's constant.

The free energy $\Delta G_0$ equals -128.9 kJmol$^{-1}$ obtained by extrapolation at ambient temperature [14,15]. When $n$ equals three equiv/mole, $E$ was deduced to be about +0.44 V [2]. The value of the experimental open-circuit potential obtained with a Li electrode covered by a Li$_3$N thick film was about +0.36V. The reason for the discrepancy between the expected and experimental values can be explained by the following experiments.

The open-circuit potential of the Li/Li$_3$N electrode versus the reference Li electrode depends on the thickness of the lithium nitride film, the immersion time in the solution, and/or the
polarization conditions. For example, as shown in Fig. 5-8, different Li/Li$_3$N electrodes (formed after 20 and 40 minutes in the nitrogen atmosphere) give different open-circuit potentials just after their immersion in the solution. Besides, a significant decrease in the potential can be observed during the immersion time, for example, from 350 to about 20 mV after 12 hours, becoming stable at 10 mV after 48 hours of immersion. The open-circuit potential of the Li/Li$_3$N electrode depended on its polarization history, as shown in Figs. 5-9 and 5-10. A cathodic deposition or an anodic dissolution with low current and charge densities led to a decrease of the electrode potential measured after the interruption of polarization.

The potential behavior of the Li/Li$_3$N electrode cannot be explained by a variation of the stoichiometry of lithium nitride especially to a loss or gain of lithium into the lattice of this compound. Besides, there is no evidence of decomposition of Li$_3$N even under high anodic polarization. In fact, this potential behavior can be easily understood when considering the slow filling of the pores of the lithium nitride film by the organic electrolyte. The measured potential is determined by lithium and lithium nitride as a function of their respective areas in contact with the organic electrolyte.

5.2.2 Electrode-Impedance Behavior

The analysis of impedance data by Cole-Cole and Bode plots, as
shown in Figs. 5-11 through 5-14, demonstrates the existence of two types of impedances. According to the compact film model, the total resistance can be separated into two components: the transcrystalline resistance $R_t$ in the high-frequency range, and the intercrystalline resistance $R_i$ in the low-frequency range. Taking into account solution resistance of $15 \, \Omega \text{cm}^2$, the total resistance of the lithium nitride film is between 200 and 325 $\Omega \text{cm}^2$, respectively, when formed after 20 and 40 minutes of exposure in a pure nitrogen atmosphere. For a minimum thickness of $10^{-2} \text{cm}$ (see section 5.1.2) for the film leading to the minimum conduction resistance of 200 $\Omega \text{cm}^2$, the transcrystalline conductivity $\sigma_t$ can be evaluated at $2.8 \times 10^{-4} \, \Omega^{-1} \text{cm}^{-1}$ ($R_t = 35 \, \Omega \text{cm}^2$), and the intercrystalline conductivity $\sigma_i$ can be evaluated at $6 \times 10^{-5} \, \Omega^{-1} \text{cm}^{-1}$ ($R_i = 165 \, \Omega \text{cm}^2$). These values, which are between the values observed for sinters [7] and those observed for single crystals [6], are certainly overestimated (see Table 5-2). The fact that the different semicircles have their centers far below the real axis, with a depression parameter of about 0.3, is characteristic of a large dispersion in the time constants related to the dielectric and resistive properties of the lithium nitride film. The intercrystalline capacitance $C_i$, deduced from the semicircle in the low-frequency range, is between 1 and 0.05 $\mu \text{F/cm}^2$, decreasing with increasing thickness of the polycrystalline film. A study of the Bode plots does not permit one to define the preceding observations more exactly, because of the limitations of the frequency range.
available for the experimental cell.

The study of the impedance behavior of the Li/Li$_3$N electrode as a function of different parameters, such as immersion time and polarization conditions, permits one to observe a significant increase in apparent conductivity of the lithium nitride film formed at ambient temperature. Figures 5-15 and 5-16 show the change of the impedance diagrams obtained with different electrodes immersed in the organic electrolyte for 48 hours. The apparent conduction impedance is reduced, but a diffusion impedance can be detected in the low-frequency range. Figures 5-17 and 5-18 show that, for different charge and current densities, a cathodic polarization as well as an anodic polarization leads to a decrease in the conduction impedance. The diffusion impedance appears only for a lithium deposit and increases with the charge density. Besides, a simple cycling, as shown in Figs. 5-19 and 5-20, leads to successive decreases in the electrode impedance, an effect observed under various polarization conditions. Nevertheless, the Li/Li$_3$N electrodes appear unsuitable for the continued cycling of lithium, as shown in Figs. 5-21 and 5-22. The cathodic deposition after five cycles leads to a very small impedance, while the subsequent anodic dissolution leads to a large impedance. The impedance behavior of the Li/Li$_3$N electrode cannot be explained by the compact film model simply as a variation of the different conductivities in order to explain the influence of the immersion time and polarization conditions. The porous-film model seems to be much more useful for
understanding the origin of the decrease of the total impedance observed in all experimental conditions. As demonstrated by mercury porosimetry (see section 5.1.3), the polycrystalline lithium nitride film formed at ambient temperature is a porous material with many very small interparticle voids or micropores. Thus, when considering a slow filling of the micropores of the material by the organic electrolyte, the influence of immersion time and polarization conditions on the evolution of the resulting electrode impedance becomes understandable. During the cycling, the impedance behavior can be complicated by the presence of the decomposition products of the organic electrolyte inside the micropores or, eventually, on the surface of the lithium nitride electrode.

In principle, all the information about the porous Li/Li₃N electrode can be derived by fitting the curve of its impedance spectrum to the general equation of the total impedance. In practice, however, when considering the number of parameters (more than 7 for the analysis of a 3-dimensional system, as shown in Appendix IV), the curve-fitting technique is not accurate enough and unique. Thus, at this time it is only possible to demonstrate that the porous-layer model provides a reasonable model for the electrode. In an attempt to predict the evolution of the impedance behavior as a function of the porosity of the porous material, the computerized impedance diagrams were generated by assuming arbitrary and/or experimental values for the different parameters. The set of parameter values presented in Table 5-3 has been used to explain the
properties of a thin lithium nitride film on the lithium electrode. This condition means that the fraction \((1-\Theta)\) of the surface area covered by the liquid electrolyte, and the number \(n\) of micropores in the solid electrolyte are relatively small compared to those determined in a thick porous lithium nitride (see Table 5-2). Besides, the resistance of the liquid phase is assumed to be that of the molar solution of lithium perchlorate in propylene carbonate, [16,17] while the impedance of the solid phase is supposed to be that of polycrystalline sinters of lithium nitride[7]. The impedance of the pore base can be defined by the impedance of the lithium electrode in presence of the same organic electrolyte. [16] The impedance of the pore wall can be represented by a large Faradaic impedance placed in parallel with the double layer capacitance. [8] Besides, it is necessary to remember that the difference of potential of lithium nitride versus lithium is not taken into account for the study of the transmission-line model.

As shown in Figs. 5-23 through 5-25, the computer-generated impedance diagrams in the complex plane can be defined over the whole frequency range for similar shape and size as the experimental diagrams (see Figs. 5-11 through 5-14) when a large dispersion parameter \(\alpha = 0.3\) is used for the intercrystalline impedance of lithium nitride. The overestimation of the transcristalline and intercrystalline conductivities observed earlier appears with the porous-film model as due to a misinterpretation of the impedance diagrams by the compact-film model. The apparent conductivities are
due to the competition between the conductivities of the liquid and solid phases involved in the system. An increase of the fraction $(1-\theta)$ and/or of the number $n$, which both are related to the porosity of the film, as shown in Fig. 5-23 and 5-24, leads to a decrease of the total electrode impedance. Thus, the change of the impedance observed as a function of different factors, such as the immersion time and polarization conditions, can be explained by a change of the Li surface area in contact with the solution through the $\text{Li}_3\text{N}$ film. On the other hand, the diffusion process, which can appear after a cathodic polarization or after a long immersion, can be due to a slight concentration gradient in the surface layer formed on the pore base in contact with the solution, as shown in Fig. 5-25. Finally, as shown in Fig. 5-26, the decrease of the electrode impedance observed during the cycling of lithium can also be explained by a decrease of the pore-wall impedance.

CONCLUSION

Lithium nitride has been studied as a possible solid-electrolyte interphase between the lithium electrode and a classical organic electrolyte, the molar solution of lithium perchlorate in propylene carbonate. The lithium/lithium nitride electrode has been obtained by exposing lithium in a pure nitrogen atmosphere at ambient temperature. The morphological study by scanning electron microscopy and mercury porosimetry has
demonstrated that the preparation procedure leads to the formation of a polycrystalline porous lithium nitride film. The kinetic study by electrode impedance spectroscopy has shown that the impedance behavior of the Li/Li3N electrode can be interpreted by the porous-film model deduced from the transmission line model by taking into account the impedances of the Li3N film and the Li backing electrode.

The porous lithium nitride film has been found to be unsuitable for cycling lithium, probably because the lithium electrode remains in contact with the electrolyte through the micropores. Nevertheless, lithium nitride remains a possible candidate material for protective films on lithium if it can be obtained as a very thin and compact film because of its apparent stability in propylene carbonate-based electrolytes.

ACKNOWLEDGMENTS

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The authors wish to thank Mr. Joseph Katz for his help and suggestions for the use of differential and lock-in amplifiers needed for the electrode-impedance spectroscopy.
References


3. F.J. Schwager and R.H. Muller, LBL-13618.


16. J.G. Thevenin and R.H. Muller, LBL-20660.


Table 5-1. Procedure used to determine the density of the Li$_3$N samples.

<table>
<thead>
<tr>
<th>Line*</th>
<th>Item</th>
<th>Formula*</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Diameter of sample</td>
<td>(cm)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>(2)</td>
<td>Length of sample</td>
<td>(cm)</td>
<td>0.65</td>
<td>0.71</td>
<td>0.70</td>
</tr>
<tr>
<td>(3)</td>
<td>Volume of sample</td>
<td>(cm$^3$)</td>
<td>0.04590</td>
<td>0.05016</td>
<td>0.04945</td>
</tr>
<tr>
<td>(4)</td>
<td>Weight of sample</td>
<td>(g)</td>
<td>0.04269</td>
<td>0.04916</td>
<td>0.04956</td>
</tr>
<tr>
<td>(5)</td>
<td>Density of Porous Li$_3$N.</td>
<td>(g/cm$^3$)</td>
<td>(4)/(3)</td>
<td>0.930</td>
<td>0.980</td>
</tr>
<tr>
<td>(6)</td>
<td>Weight of sample filled with mercury.</td>
<td>(g)</td>
<td>0.17748</td>
<td>0.19535</td>
<td>0.17721</td>
</tr>
<tr>
<td>(7)</td>
<td>Weight of mercury in sample.</td>
<td>(g)</td>
<td>0.13479</td>
<td>0.14619</td>
<td>0.12765</td>
</tr>
<tr>
<td>(8)</td>
<td>Volume of mercury in sample.</td>
<td>(cm$^3$)</td>
<td>0.00995</td>
<td>0.01079</td>
<td>0.00942</td>
</tr>
<tr>
<td>(9)</td>
<td>Volume of pores and interparticle voids.</td>
<td>(cm$^3$)</td>
<td>(8)</td>
<td>0.00995</td>
<td>0.01079</td>
</tr>
<tr>
<td>(10)</td>
<td>Volume of compact material.</td>
<td>(cm$^3$)</td>
<td>(3)-(9)</td>
<td>0.03595</td>
<td>0.03937</td>
</tr>
<tr>
<td>(11)</td>
<td>Density of compact Li$_3$N.</td>
<td>(g/cm$^3$)</td>
<td>(4)/(10)</td>
<td>1.187</td>
<td>1.248</td>
</tr>
</tbody>
</table>

*Use the number in parentheses for reference in the calculations described under "Formula."
Table 5-2. Selected Properties of Lithium Nitride.

<table>
<thead>
<tr>
<th>Conductivity, Q⁻¹ cm⁻¹</th>
<th>Monocrystal</th>
<th>Polycrystalline sinter</th>
<th>Our work (apparent values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ//</td>
<td>1.2 x 10⁻³</td>
<td>6 x 10⁻⁴</td>
<td>2.8 x 10⁻⁴</td>
</tr>
<tr>
<td>σ⊥</td>
<td>1 x 10⁻⁵</td>
<td>3 x 10⁻⁶</td>
<td>6 x 10⁻⁵</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density, g/cm³</th>
<th>Monocrystal</th>
<th>Polycrystalline sinter</th>
<th>Our work porous dp = 0.97</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.29</td>
<td>1.26</td>
<td></td>
</tr>
</tbody>
</table>

Parameters of the porous film (limiting values)

Fraction (1-θ) of the surface area of the lithium electrode free of lithium nitride film, knowing that the fraction θ is given by the ratio between the densities of the porous and compact lithium nitride.

θ = dp/dc = 0.8
(1-θ) = 0.2

Number n of micropores per unit surface area (A = 1 cm²) for a given pore radius (r = 150 Å) of the micropores, knowing that

nπr² = (1-θ)A
n = 3 x 10¹⁰
Table 5-3. Values for the parameters used in the transmission line model. Computer-generated impedance diagrams shown in Figs. 5-23 through 5-26.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction of the electrode surface covered by the solid phase.</td>
<td>( \theta = 0.95 )</td>
</tr>
<tr>
<td>Number of pores per unit area filled by the liquid phase.</td>
<td>( n = 10^4 )</td>
</tr>
<tr>
<td>Thickness of the porous electrode.</td>
<td>( L = 10^{-2} \text{ cm} )</td>
</tr>
<tr>
<td>Electrolyte resistance.</td>
<td>( R_q = 15 \ \Omega \text{cm}^2 )</td>
</tr>
<tr>
<td>Resistance of the liquid phase (for a thickness of 0.01 cm)</td>
<td>( R_L = 2 \ \Omega \text{cm}^2 )</td>
</tr>
</tbody>
</table>
| Impedance of the solid phase \( ZS \) (for a thickness of 0.01 cm) | \( Z_T \) \{ \begin{align*} 
Z_T & = 15 \ \Omega \text{cm}^2 \\
CT & = 1 \ \mu\text{F/cm}^2 
\end{align*} \} \\
\{ \begin{align*} 
Z_I & = 3000 \ \Omega \text{cm}^2 \\
CI & = 1 \ \mu\text{F/cm}^2 
\end{align*} \} |
| Impedance of the pore base \( ZB \).                          | \( Z_B \) \{ \begin{align*} 
RB & = 10 \ \Omega \text{cm}^2 \\
CB & = 10 \ \mu\text{F/cm}^2 
\end{align*} \} |
| Impedance of the pore wall \( ZP \).                          | \( Z_P \) \{ \begin{align*} 
RP & = 5000 \ \Omega \text{cm}^2 \\
CP & = 25 \ \mu\text{F/cm}^2 
\end{align*} \} |
Figure Captions

Fig. 2-1. a) Schematic representation of Li₃N. Two Li(2)₂N layers are shown, separated by a Li(1) layer (from Ref. [2], Fig. 10).

b) Projection of Li₃N along the C-axis. Li(2) and N atoms lie in the Li₃N layer for the position z=0 (from Ref. [2], Fig. 30).

Fig. 2-2. Semilogarithmic plot of the ionic bulk conductivity of lithium nitride as a function of the inverse absolute temperature.

(a) Li₃N monocrystal, (from Ref. [17], Fig. 2).

\[ \sigma_{\perp} : (\square) \text{ dc, } (\triangle) \text{ ac perpendicular to the c-axis}; \]

\[ \sigma_{//} : (\blacksquare) \text{ dc, } (\triangle) \text{ ac parallel to the c-axis}. \]

(b) Li₃N Sinter (from Ref. [8], Fig. 4).

\[ \sigma_i : (0), \text{ intercrystalline conductivity}, \]

\[ \sigma_t : (\square), \text{ transcrystalline conductivity}. \]
Fig. 3-1. Schematic view of a compact polycrystalline material covering a metal electrode, with the elementary impedance circuit shown.

Fig. 3-2. (a.) Equivalent circuit for compact-layer model of a polycrystalline material. (b.) Impedance diagram in the complex plane.

Fig. 3-3. Schematic view of a porous polycrystalline material covering a metal electrode, showing the elementary impedance circuit.

Fig. 3-4. (a.) Equivalent circuit of the transmission-line model in discreet form. (b.) Impedance diagram in the complex plane.

Fig. 4-1. Schematic view of the electrolytic cell.

Fig. 4-2. Electrode-impedance setup. (The reference, voltage* and current* are needed only for use of the internal electrometer monitor and current follower).

Fig. 5-1. (a) SEM of the surface of a thin lithium nitride
film. (b) SEM of the cross section of a thin lithium nitride film. (c) SEM of the surface of a thick lithium nitride film.

Fig. 5-2. Crystallographic study of the body-centered cubic lattice of lithium: (a) (001) plane, (b) (110) plane.

Fig. 5-3. Crystallographic study of the hexagonal lattice of lithium nitride: (a) (0001) plane, (b) (1000) plane.

Fig. 5-4. Evolution of cumulative pore-volume as a function of applied mercury pressure or pore radius, according to the Washburn equation.

Fig. 5-5. Evolution of differential pore-volume density as a function of pore radius.

Fig. 5-6. Evolution of differential pore-surface density as a function of pore radius.

Fig. 5-7. Evolution of differential pore-length density as a function of pore radius.
Fig. 5-8. Evolution of the open-circuit potential (OCP) for the Li₃N film as a function of the immersion time in the solution. Influence of the time of exposure to N₂ atmosphere: (a) 20 minutes; (b) 30 minutes; (c) 40 minutes.

Fig. 5-9. Study of the OCP of the Li/Li₃N electrode as a function of the polarization conditions (Electrode formed after 1 hour): (a) OCP just after immersion; (b) potential during cathodic polarization (current density 0.5 mA/cm²); (c) OCP just after Li cathodic deposition (charge density 0.5 C/cm²).

Fig. 5-10. Study of the OCP of the Li/Li₃N electrode as a function of the polarization conditions (electrode formed after 1 hour): (a) OCP just after immersion, (b) potential during anodic polarization (current 0.5 mA/cm²), (c) OCP just after Li anodic dissolution (charge density 0.5 C/cm).

Fig. 5-11. Influence of formation time of the Li/Li₃N electrode on impedance diagram. Reference diagram at the open-circuit potential.

Formation time = 20 min. (a) Cole-Cole
Plot; (b,c) Bode plots, modulus and angle.

Fig. 5-12. Influence of formation time of the Li/Li$_3$N electrode on impedance diagram. Reference diagram at the open-circuit potential. Formation time = 25 min. (a) Cole-Cole plot; (b,c) Bode plot, modulus and angle.

Fig. 5-13. Influence of formation time of the Li/Li$_3$N electrode on impedance diagram. Reference diagram at the open-circuit potential. Formation time = 30 min. (a) Cole-Cole plot; (b,c) Bode plot, modulus and angle.

Fig. 5-14. Influence of formation time of the Li/Li$_3$N electrode on impedance diagram. Reference diagram at the open-circuit potential. Formation time = 40 min. (a) Cole-Cole plot; (b,c) Bode plot, modulus and angle.

Fig. 5-15. Influence of immersion time in the organic electrolyte on impedance diagram. Evolution of the impedance diagram at the open-circuit potential. (a) reference diagram (initial time); (b) diagram after
24 hr.; (c) diagram after 48 hr.

Fig. 5-16. Influence of immersion time in the organic electrolyte on impedance diagram. Evolution of the impedance diagram at the open-circuit potential. (a) reference diagram (initial time); (b) diagram after 24 hr.; (c) diagram after 48 hr.

Fig. 5-17. Influence of polarization conditions on impedance diagram. Evolution of the impedance diagram during cathodic polarization with a current density of $-0.25 \text{ mA/cm}^2$. (a) reference diagram (open-circuit potential); (b) diagram with a charge density of 1 C/cm$^2$; (c) diagram with a charge density of 5 C/cm$^2$.

Fig. 5-18. Influence of polarization conditions on impedance diagram. Evolution of the impedance diagram during anodic polarization with a current density of 0.25 mA/cm$^2$. (a) reference diagram (open-circuit potential); (b) diagram with a charge density of 1 C/cm$^2$; (c) diagram with a charge density of 5 C/cm$^2$. 
Fig. 5-19. Influence of a simple cycling operation on impedance diagram. Evolution of the impedance diagram at the open-circuit potential. Current density $0.5 \text{ mA/cm}^2$, charge density $1 \text{ C/cm}^2$. (a) reference diagram (before cycling); (b) diagram after Li cathodic deposition; (c) diagram after Li anodic dissolution.

Fig. 5-20. Influence of a simple cycling operation on impedance diagram. Evolution of the impedance diagram at the open-circuit potential. Current density $0.5 \text{ mA/cm}^2$, charge density $5 \text{ C/cm}^2$. Reference diagram (a) before cycling; (b) diagram after Li cathodic deposition; (c) diagram after Li anodic dissolution.

Fig. 5-21. Influence of immersion time and cycling conditions on impedance diagram at the open-circuit potential. Reference diagram in Fig. 15c. Current density $0.5 \text{ mA/cm}^2$, charge density $1 \text{ C/cm}^2$. (a) after first cathodic deposition; (b) after first anodic dissolution; (c) after second cathodic deposition; (d) after second anodic dissolution; (e) after fifth cathodic deposition; (f) after fifth anodic dissolution.
Fig. 5-22. Influence of immersion time and cycling conditions on impedance diagram at the open circuit potential. Reference diagram in Fig. 16c. Current density 1 mA/cm². (a) after first cathodic deposition; (b) after first anodic dissolution; (c) after second cathodic deposition; (d) after second anodic dissolution; (e) after fifth cathodic deposition; (f) after fifth anodic dissolution.

Fig. 5-23. Computer-generated impedance diagram based on the porous-film model (transmission-line model). Influence of the fraction \( \Theta \) of surface area covered by the solid phase.
(a) \( \Theta = 0.95 \); (b) \( \Theta = 0.925 \); (c) \( \Theta = 0.90 \)

Fig. 5-24. Computer-generated impedance diagram based on the porous-film model (transmission-line model). Influence of the number \( n \) of micropores per unit surface area.
(a) \( n = 10^4 \); (b) \( n = 10^5 \); (c) \( n = 10^6 \)

Fig. 5-25. Computer-generated impedance diagram based on the porous-film model (transmission-line model). Influence of the pore-base impedance (Warburg coefficient) on the total impedance.
(a) $KB = 0$; (c) $KB = 0.1$; (c) $KB = 0.2$

Fig. 5-26. Computer-generated impedance diagram based on
the porous-film model (transmission-line model).
Influence of the pore-wall impedance on the total
impedance.
(a) $RP = 5000$; (b) $RP = 500$; (c) $RP = 50 \Omega^{-1} cm^{-1}$
Li (2)
Li (1)
Li$_2$N
Li
Li$_2$N

\[ z = 1/2 \]
\[ z = 0 \]

\[ N \quad z = 0 \]

Fig. 2-1
Temperature (°C)

Log $\sigma \times T$ ($\Omega^{-1} \text{ cm}^1 \times K$)

Inverse temperature $10^3/T \times (K^{-1})$

Fig. 2-2
Fig. 3-4
Oscillator
(frequency range $10^6 - 10^{-3}$ Hz)

Potentiostat-galvanostat
(galvanostatic mode)

Electrometer monitor
Current follower

Storage oscilloscope
Voltage
Current

Voltage
Current

Fig. 4-2
Fig. 51a
Fig. 5-2
Fig. 5-3
Pressure $P$ (kg/cm$^2$)

Cumulative pore volume $V$ (cm$^3$)

Pressure $P$ (psia)

Pore radius $R$ (Å)

Fig. 5-4
D\textsubscript{v} (R) = \frac{P}{R} \frac{dV}{dP}

Differential pore volume density 

\( D\textsubscript{v} (R) \) (arbitrary units)

Pore radius \( R \) (Å)

Fig. 5-5
\[ D_s(R) = \frac{P \, dV}{R^2 \, dP} \]

Fig. 5-6
\[ D_L (R) = \frac{P \, dV}{R^3} \, dP \]

**Fig. 5-7**
Fig. 5-9
Fig. 5-12
Fig. 5-13
Fig. 5-14
Fig. 5-15
Fig. 5-16
Fig. 5-17
Fig. 5-18
Fig. 5-19
Fig. 5-20
Fig. 5-22
Fig. 5-23
Fig. 5-24
Fig. 5-25
Fig. 5-26
APPENDIX I. Conduction Models for Solid Electrolytes

The metal-electrode/solid-electrolyte interface can be modeled differently according to the nature of the metal electrode and the hypotheses used for the mobile ions in the solid electrolyte.

The electrodes are usually discussed in terms of blocking and nonblocking electrodes. A blocking electrode is one into which the mobile ion cannot penetrate. An example is a nickel substrate for a lithium nitride film: the mobile lithium ions in the solid electrolyte cannot penetrate the nickel atoms of the electrode. The opposite situation is a nonblocking electrode. An example is a lithium electrode on a lithium nitride film. In this case, the mobile lithium ions from the solid electrolyte can discharge at a very high rate toward the lithium electrode by crossing the electrode/electrolyte interface and penetrating the metal.

The mobile ions are considered to be either point charges or finite-size species. In the point-charge model of MacDonald [18-21], all the mobile ions in the solid electrolyte are considered as point charges for which double-layer effects are neglected. The mobile ions are able to approach the electrode to within any distance, no matter how small. In the finite-ion-size model of Armstrong [22-24], the solid electrolyte consists of immobile anions, and the cations are all equivalent and mobile. In this case the ionic size is taken into account, since the distance of closest approach of the ion to the electrode surface is controlled by the ionic radius.
The point-charge and finite-ion-size models are discussed in greater detail below.

1.1 Point-Charge Model

For a nonblocking electrode, the double-layer capacitance is zero because of the infinitely rapid discharge rate of the charged species across the electrolyte/electrode interface.

The equivalent circuit and impedance spectrum predicted by MacDonald are shown in Fig. A1-1 (a and b). The conduction process is represented by a simple circuit in which the geometric capacitance $C_g$ and the bulk resistance $R_b$ are:

$$C_g = \varepsilon_r \varepsilon_0 \frac{A}{L}$$

$$R_b = \frac{L}{A\sigma},$$

where $L$ is the thickness and $A$ is the surface area, $\varepsilon_r$ the permittivity ($\varepsilon_0$ permittivity of vacuum) and $\sigma$ is the conductivity of the solid electrolyte. Thus, the impedance diagram in the complex plane is a semicircle over the whole frequency range. The parameter $\omega^*$, the radial frequency at the maximum of the semicircle, is related to $C_g$ and $R_b$ by:

$$R_b C_g \omega^* = 1.$$
For a blocking electrode, the double-layer capacitance depends on the conditions of the system [8]. For example, for a blocking electrode, this capacitance can be defined as:

\[ C_{dl} = \frac{\varepsilon_r \varepsilon_0 A}{L_D} \cosh \left( \frac{V_e}{2kT} \right), \]

where \( L_D \) is the Debye length and \( V_e \) is the applied potential. The equivalent circuit and impedance diagram are given in Fig. A1-1 (c and d) to show the location of the double-layer capacitance and the effect on the impedance data.

### 1.2 Finite-Ion-Size Model

For nonblocking electrodes, the structure of the double layer depends on the size of the exchange current for cation transfer between the metal and the cations in the first layer adjacent to the surface. In this model, the metal surface is assumed to be adjacent to a layer of cations and anions (layer 1), which in turn is adjacent to another layer of anions and cations (layer 2). Thus, the equivalent circuit is made of two RC circuits placed in series, as shown in Fig. A1-2 (a and b). The charge-transfer resistance \( R_{ct} \) represents the charge-transfer process, assuming the reaction consists of one step. The double-layer capacitance \( C_{dl} \) is determined by \( \varepsilon_r' \), the relative permittivity of the electrode/first-layer region, and by \( d \), the distance between the charge centers of the cations in the first layer and the electrode surface:
The bulk resistance $R_b$ is related to the conductive properties of the solid electrolyte. But the geometric capacitance $C_g$ is not placed across the total cell and is thought of as arising from the summation of the capacitances between layers 1 and 2 and the other layers along the distance $(L-d)$, according to:

$$C_g = \varepsilon_r \varepsilon_0 \frac{A}{(L-d)}.$$

The impedance diagram in the complex plane is two semicircles, each covering a different frequency range. The parameter $\omega_1$, the frequency at the maximum of the semicircle in the high-frequency range, is related to the conduction process and defined by:

$$R_b C_g \omega_1 = 1.$$

The parameter $\omega_2$, the frequency at the maximum of the semicircle in the low-frequency range, is related to the charge-transfer process and defined by:

$$R_{ct} C_{d1} \omega_2 = 1.$$

When the charge-transfer resistance for cation transfer between the electrode and electrolyte is less than that between adjacent layers in
the bulk of the solid electrolyte, the charge-transfer impedance becomes
negligible, and the electrochemical behavior of the system becomes
identical to that predicted by the point-charge model.

For a blocking electrode, the double-layer capacitance, which is
caus by a deviation from electroneutrality between the metal electrode
and the first layer, will vary with the applied potential. The equivalent
circuit and impedance diagrams are shown in Fig. Al-2 (c and d). The
double-layer capacitance is placed in series with the circuit of the
parallel network $C_g/R_b$, the geometric capacitance and bulk resistance.
The impedance spectrum exhibits a semi-circle in the high-frequency range
and a straight line in the low-frequency range.

Appendix II. Analysis of the Compact-Film Model

In a polycrystalline anisotropic solid electrolyte, various
orientations will be adopted by the individual particles. As a result,
the conductance of each particle in a direction perpendicular to the
electrodes will be different. The differing orientations of the $n$
particles will lead to an average value of the dielectric and resistive
properties of the polycrystalline sample. The total impedance for $n$
different RC circuits placed in series for each type of impedance is:

$$Z_T(\omega) = \sum_{k=1}^{n} \frac{R^k}{1 + (j\omega R^k C^k)} = \sum_{k=1}^{n} \frac{R^k}{1 + (j\omega / \omega^k)}.$$
where $\omega^k$ is the angular frequency corresponding to the time constant of an elementary RC circuit \((R^k C^k \omega^k = 1)\).

An elegant solution to this problem was given by Cole and Cole [9] by taking into account a depression parameter $\alpha$ and a pseudo-RC equivalent circuit:

$$Z_\alpha = \frac{R}{1 + (j\omega RC)^{1-\alpha}} = \frac{R}{1 + (j\omega/\omega_0)^{1-\alpha}}$$

where $\omega_0$ represents the angular frequency corresponding to the time constant of the pseudo-RC equivalent circuit. The impedance diagram in the complex plane, which is a semicircle centered on the real axis when $\alpha=0$, becomes a semicircular arc whose center lies below the real axis at an angle $\Theta = \alpha\pi/2$. The real and imaginary components of the Cole-Cole impedance are defined as follows:

$$Z_\alpha(\omega) = Z'_\alpha - j Z''_\alpha$$

$$= R \left\{1 + (\omega RC)^{1-\alpha} \left[\cos(1-\alpha)\pi/2 - j \sin(1-\alpha)\pi/2\right]\right\}$$

$$\left[1 + (\omega RC)^{1-\alpha} \cos(1-\alpha)\pi/2\right]^2 + \left[(\omega RC)^{1-\alpha} \sin(1-\alpha)\pi/2\right]^2$$

Figure A2-1 shows the equivalent circuit where the transcrystalline
and intercrystalline impedances can be defined separately for each particle. Thus, the equivalent circuit corresponding to a chain of particles between the electrodes is two series of RC circuits. The first series is related to the resistance $R_{t}^{n-1}$ and the capacitance $C_{t}^{n-1}$ inside particle (n-1). The second series is determined by the intercrystalline resistance $R_{i}^{n-1}$ and the capacitance $C_{i}^{n-1}$ between particle (n-1) and particle (n).

The equivalent circuit of a polycrystalline anisotropic solid electrolyte can be represented by two pseudo-RC circuits corresponding to the transcrystalline and intercrystalline impedances:

$$Z_{T}(\omega) + \frac{R_{t}}{1 + (j\omega R_{t} C_{t})(1-\alpha_{t})} + \frac{R_{i}}{1 + (j\omega R_{i} C_{i})(1-\alpha_{i})}$$

where $\alpha_{t}$ and $\alpha_{i}$ are the depression parameters related to the dispersion of the time constants in the respective pseudo-RC equivalent circuits.

Appendix III. Analysis of the Porous-Film Model

Although details of the transmission-line derivation have been published previously by Park and MacDonald [11], they are reproduced here since the model forms the basis of the study of the impedance behavior of porous electrodes of finite thickness. As a simplifying assumption for the transmission-line model, the film is considered to have a homogeneous
porous structure with straight, parallel, and cylindrical pores having the same pore base and a constant composition for the pore wall.

Thus, two phases must be considered:

(1) The liquid phase filling the pores is the electrolyte. An average liquid-phase resistance per unit pore length, $R_1/L$, is assumed. The radial and axial concentration gradients of the electrolyte in the pores are neglected.

(2) The solid-phase is the material studied. An average solid-phase impedance per unit pore length, $Z_s/L$, is defined. A uniform active material is assumed to line the pore walls.

With these hypotheses, the impedance behavior of the electrode is determined by two types of interfacial impedances:

(1) The impedance occurring on the pore base, $Z_b$, which is the impedance of the electrode/electrolyte interface.

(2) The admittance occurring on the pore wall, per unit pore length, $1/Z_p L$, which is the admittance of the material/electrolyte interface.

The equivalent electrical circuit for a single pore is represented by a finite form of the transmission-line model, as shown in Fig. A3-1. The thickness of the layer is determined along the x axis from 0 at the contact with the mouth of the pore to L at the contact with the base of the pore. The current ($i*$) and potential ($e*$) distributions within the porous system and the total impedance $Z_T$ can be derived by the application of the circuit-analysis equations for a typical discrete
unit, assuming that the indices (*) are given for the solid (s) and liquid (l) phases, respectively. On the other hand, I and I* are the total current in the electrode and the global current flowing across the electrode at the pore base. E is the potential difference across the pore-wall/liquid-electrolyte interface. Thus,

\[ I = i_s + i_l, \quad (1) \]
\[- dE_s = i_s (Z_s/L) \, dx, \quad (2) \]
\[- dE_l = i_e (R_l/L) \, dx, \quad (3) \]
\[ E = e_s - e_l = di_s (Z_p L)/dx = di_l (Z_p L)/dx. \quad (4) \]

Using equations (1) through (4), and assuming \( Z_p, Z_s, \) and \( R_l \) to be independent of \( x \), the following differential equations can be obtained:

\[ \frac{d^2 i_s}{dx^2} - \gamma i_s + \frac{R_l}{Z_p L^2} \quad I = 0 \quad (5) \]
\[ \frac{d^2 i_l}{dx^2} - \gamma i_l + \frac{Z_s}{Z_p L^2} \quad I = 0 \quad (6) \]
\[ \frac{d^2 E}{dx^2} - \gamma E = 0 \quad (7) \]

where
\[ \gamma = \frac{Z_s + R_l}{Z_p L^2}. \]
The three second-order differential equations using \( i_s, i_1, \) and \( E \) must be solved subject to the following boundary conditions:

(mouth of pore) \( x = 0 \):
\[
i_1 = I, \quad i_s = 0, \quad \frac{dE}{dx} = I \left( \frac{R_1}{L} \right); \quad (8)
\]

(base of pore) \( x = L \):
\[
i_1 = I^*, \quad i_s = I - I^*, \quad E = I^* Z_b. \quad (9)
\]

The solutions to differential equations (5) and (6) are the following:

\[
i_s = c_1 \exp(- \gamma^{1/2} x) + c_2 \exp(\gamma^{1/2} x) + \frac{R_1 I}{\gamma Z_p L^2} \quad (10)
\]

\[
i_1 = -c_1 \exp(- \gamma^{1/2} x) - c_2 \exp(\gamma^{1/2} x) + \frac{I}{Z_p L^2} \quad (11)
\]

with

\[
c_2 = \frac{1}{2 \sinh(\gamma^{1/2} L)} \left( \frac{Z_s I + R_1 I \exp(- \gamma^{1/2} L)}{Z_p L^2} - I^* \right), \quad (12a)
\]

\[
c_1 = -c_2 - \frac{R_1 I}{\gamma Z_p L^2} = \frac{-1}{2 \sinh(\gamma^{1/2} L)} \left( \frac{Z_s I + R_1 I \exp(\gamma^{1/2} L)}{\gamma Z_p L^2} - I^* \right); \quad (12b)
\]

and the solution to differential equation (7) is the following:
\[ E = c_1' \exp(-\gamma^{1/2}x) - c_2' \exp(\gamma^{1/2}x), \quad (13) \]

with

\[ c_2' = \frac{1}{2 \cosh (\gamma^{1/2}L)} \left( \frac{R_1 I \exp(-\gamma^{1/2}L)}{\gamma^{1/2}L} - 1^* Z_b \right) \quad (14a) \]

\[ c_1' = \frac{-1}{2 \cosh (\gamma^{1/2}L)} \left( \frac{R_1 I \exp(\gamma^{1/2}L)}{\gamma^{1/2}L} + 1^* Z_b \right) \quad (14b) \]

The potential drop between the base of the pore and the mouth of the pore is given by:

\[ V = e_1(x=0) - e_s(x=L) = I_n Z_T \quad (15) \]

\[ = -E(x=L) + \int_0^L (R_1/L) i_1 \, dx = -E(x=0) + \int_0^L (Z_s/L) i_s \, dx \]

where \( Z_T \) is the total impedance and \( n \) is the number of parallel, straight, single one-dimensional pores. Hence, the following equation represents the total impedance:
\[ Z_T = \frac{1}{n} \left\{ \left( \frac{Z_S R_1}{Z_S + R_1} \right) + \frac{2 \gamma^{1/2} Z_S R_1 + \gamma^{1/2} (Z_S^2 + R_1^2) C + \delta R_1^2 S}{L \gamma^{1/2} (Z_S + R_1) (\gamma^{1/2} S + \delta C)} \right\} \]  \hspace{1cm} (16)

where \[ \gamma = \frac{Z_S + R_1}{Z_b L^2} \] , \[ \delta = \frac{Z_S + R_1}{Z_b L} \] ,

and \[ C = \cosh (\gamma^{1/2} L) \] , \[ S = \sinh (\gamma^{1/2} L) \] .
Appendix IV. Application of the Transmission-Line Model to a Three-Dimensional System

If it is assumed that the porous film covers the electrode surface, and \((1-\Theta)\) is the fraction of the area occupied by pores, then the average area of the pore base and solid base are defined by \((1-\Theta)/n\) and \(\Theta/n\), respectively. Thus, \(R_1\) and \(Z_s\), the liquid- and solid-phase impedances, can be determined as a function of their respective specific quantities defined for planar systems \(R_L\) and \(Z_S\):

\[
R_1/L = R_L n/(1-\Theta)L,
\]

\[
Z_s/L = Z_S n/\Theta L.
\]

On the other hand, knowledge of the average dimensions of the pores, especially the pore radius, \(\pi r^2 = (1-\Theta)/n\), and the surface area of the pore wall, \(2 \pi r L\), permits one to determine \(Z_b\) and \(Z_p\) as a function of their respective specific quantities defined for planar systems \(Z_B\) and \(Z_P\):

\[
Z_b = Z_B n/(1-\Theta),
\]

\[
Z_p L = Z_P n^{1/2} / 2 \pi^{1/2} (1-\Theta)^{1/2}.
\]

The above expressions for \(Z_s\), \(R_1\), \(Z_b\) and \(Z_p\) defined for a three-dimensional system can be used easily in the general equation of
the total impedance, $Z_t$, and values of $R_L$, $Z_S$, $Z_B$, and $Z_P$ can be determined from planar-electrode impedances.

IV.1 Resistance $R_L$ of the Liquid Phase

This resistance is determined by the conductivity of the organic electrolyte used. (This resistance is different from $R_\Omega$ corresponding to the resistance of the solution in front of the electrode.)

IV.2 Impedance $Z_S$ of the Solid Phase

This impedance results from the dielectric and resistive properties of polycrystalline lithium nitride film. The equivalent circuit and impedance diagram are given by the compact-layer model, as shown in Fig. A4-1 (See Appendix II). Over the whole frequency range, the two semicircles are due to the $RT/CT$ and $RI/CI$ couplings, corresponding to the transcrystalline and intercrystalline impedances, respectively. The solid-phase impedance $Z_S$ is defined as $Z_S' - jZ_S''$, where the real $Z_S'$ and imaginary $Z_S''$ components are given by:

$$Z_S' = \frac{RT}{1 + \omega^2 RT^2 CT^2} + \frac{RI}{1 + \omega^2 RI^2 CI^2},$$

$$Z_S'' = \frac{\omega RT^2 CT}{1 + \omega^2 RT^2 CT^2} + \frac{\omega RI^2 CI}{1 + \omega^2 RI^2 CI^2},$$

in the simple case of nondispersion of the time constants. For a large
dispersion of the time constants, the solid-phase impedance is defined as a function of depression parameters $\alpha_t$ and $\alpha_i$ for the transcrystalline and intercrystalline impedances.

**IV.3 Impedance $Z_P$ of the Pore Wall**

This impedance is determined by the properties of the film/solution interface. This interface can be represented, independent of the solution resistance, by a double layer capacitance $C_P$ placed in parallel with a charge transfer resistance $R_P$. For the case of an ionic conductor, this charge transfer resistance must have a high value. The equivalent circuit and the corresponding impedance diagram determined by the $R_P/C_P$ coupling are shown in Fig. A4-2.

The pore-wall impedance $Z_P$ is defined by $Z_P' - jZ_P''$, and the real $Z_P'$ and imaginary $Z_P''$ components are given by:

\[
Z_P' = \frac{R_P}{1 + \omega^2 R_P^2 C_P^2},
\]

\[
Z_P'' = \frac{\omega R_P^2 C_P}{1 + \omega^2 R_P^2 C_P^2}
\]
IV-4 Impedance $Z_B$ of the Pore Base

This impedance is essentially due to the presence on the lithium electrode of a surface layer resulting from the decomposition products of the organic electrolyte in the presence of lithium. During the first growth of this surface layer, the electrode kinetics is essentially determined by the charge-transfer process governed by an ionic diffusion process. As shown in Fig. A4-3, independent of the electrolyte resistance, the equivalent circuit can be represented by a capacitance $C_B$, placed in parallel with a charge-transfer resistance $R_B$, and a diffusion impedance characterized by the Warburg constant $K_B$. The high-frequency semicircle in the complex plane, related to the charge-transfer process, results from the coupling $R_B/C_B$, while the low-frequency straight line, associated with the diffusion process, is defined by the Warburg constant $K_B$.

The pore-base impedance $Z_B$ is defined by $Z_B' - jZ_B''$, where the real $Z_B'$ and imaginary $Z_B''$ components are:

$$Z_B' = \frac{RB}{1 + \omega^2 R_B^2 C_B^2} + K_B \omega^{-1/2},$$

$$Z_B'' = \frac{\omega R_B^2 C_B}{1 + \omega^2 R_B^2 C_B^2} + K_B \omega^{-1/2}.$$
Figure Captions (Appendices)

Fig. A1-1. Point-charge model of a solid electrolyte: (a,b) equivalent circuit and impedance spectrum for a nonblocking electrode; (c,d) equivalent circuit and impedance spectrum for a blocking electrode.

Fig. A1-2. Finite ion size model of a solid electrolyte: (a,b) equivalent circuit and impedance spectrum for a nonblocking electrode; (c,d) equivalent circuit and impedance spectrum for a blocking electrode.

Fig. A2-1. Study of the compact-film model. (a) Equivalent circuit; (b) reduced circuit with depression parameters; according to the Cole-Cole Model.

Fig. A3-1. Study of the porous-film model. Discrete form of the equivalent circuit corresponding to the Park and McDonald Model.

Fig. A4-1. Study of the impedance $Z_S$ of the solid phase. (a) Equivalent circuit; (b) Impedance diagram.

Fig. A4-2. Study of the impedance $Z_P$ of the pore wall. (a)
Equivalent circuit; (b) Impedance diagram.

Fig. A4-3. Study of the impedance $Z_B$ of the pore base. (a) Equivalent circuit; (b) Impedance diagram.
Fig. A1-2
a) $\text{CT} \quad [\alpha_t] \quad \text{RT} \quad [\alpha_i] \quad \text{CI}$

b) $\omega_i \cdot \text{RI} \cdot \text{CI} = 1$

$\omega_t \cdot \text{RT} \cdot \text{CT} = 1$

$\omega \to \infty$

$\omega \to 0$

$Z''$

$Z'$

Fig. A4-1
Fig. A4-3
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