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Reversible Mn$^{2+}$/Mn$^{4+}$ double redox in lithium-excess cathode materials

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There is an urgent need for low-cost, resource-friendly, high-energy-density cathode materials for lithium-ion batteries to satisfy the rapidly increasing need for electrical energy storage. To replace the nickel and cobalt, which are limited resources and are associated with safety problems, in current lithium-ion batteries, high-capacity cathodes based on manganese would be particularly desirable owing to the low cost and high abundance of the metal, and the intrinsic stability of the Mn$^{4+}$ oxidation state. Here we present a strategy of combining high-valent cations and the partial substitution of fluorine for oxygen in a disordered-rocksalt structure to incorporate the reversible Mn$^{2+}$/Mn$^{4+}$ double redox couple into lithium-excess cathode materials. The lithium-rich cathodes thus produced have high capacity and energy density. The use of the Mn$^{2+}$/Mn$^{4+}$ redox reduces oxygen redox activity, thereby stabilizing the materials, and opens up new opportunities for the design of high-performance manganese-rich cathodes for advanced lithium-ion batteries.

Lithium-ion-based energy storage is becoming a pervasive technology in today’s society. Introduced in the early 1990s for use in portable electronics, it has now migrated to applications such as transportation and grid, for which energy storage needs will soon dwarf the use in electronics$^{1–2}$. Indeed, today, with electric vehicles making up about 1% of all car sales, almost half of all Li-ion batteries produced are already directed towards transportation. These new applications increase the demand for safe high-energy storage at low cost and without relying on constrained natural resources$^{3–5}$. In this context, it is remarkable that almost all Li-ion cathode materials rely on only two transition metals, Ni and Co, which are the electroactive elements in the layered-rocksalt cathode materials in the Li(Ni$_x$Mn$_{1−x}$Co)O$_2$ chemical space (NMCs)$^{3}$. On one end of this compositional spectrum, LiCoO$_2$ dominates the electronics sector, whereas Ni-rich materials are of interest for the automotive sector$^6$. Although Mn has been used in a spinel cathode$^7$, and Fe in the LiFePO$_4$ olivine$^8$, these compounds suffer from low energy density. Given the limits of energy density that can be achieved with the layered NMCs and the potential resource constraints on cobalt$^2$, it is of interest to develop high-capacity cathode materials based on other redox metals. In particular, transition metals that can exchange two electrons are of interest for their ability to create high capacity, similar to the Ni$^{2+}$/Ni$^{4+}$ couple in NMC cathodes. Low cost and low toxicity make the Mn$^{2+}$/Mn$^{4+}$ couple particularly desirable$^9$ for designing high-performance Li-ion batteries that are also inexpensive and eco-friendly.

Manganese is currently used in cathode materials, but mostly in the inert Mn$^{4+}$ state, as in NMC cathodes, or for its Mn$^{3+}$/Mn$^{4+}$ couple, as in LiMn$_2$O$_4$ spinel$^{1–3,4,7}$. More recently, Mn$^{3+}$ has been used in disordered-rocksalt-type cathodes, such as Li$_x$Mn$_2$O$_4$Nb$_2$O$_5$, in which the low capacity from Mn$^{3+}$/Mn$^{4+}$ needs to be overcome by a large amount of oxygen redox$^8$, which can trigger O loss, resulting in substantial voltage and capacity fade$^9,10$. In Li$_2$Mn$_2$O$_6$, a high initial capacity (>300 mAh g$^{-1}$) is achieved by oxidizing Mn$^{3+}$ past the standard Mn$^{3+}$/Mn$^{4+}$ redox couple, but this causes substantial voltage and capacity fade in subsequent cycles$^{11}$. In our approach, we start instead from Mn$^{3+}$ in the discharged state so that a high theoretical capacity can be obtained by oxidizing to Mn$^{4+}$ without relying on O redox. Cycling between two stable valence states of Mn, and limiting the O redox, is expected to improve the reversibility of the charge/discharge process. Reduction to Mn$^{2+}$ has been observed$^{12}$ by lithiation of amorphous Li$_x$Mn$_{2/3}$Nb$_{1/3}$O$_2$, but as this cathode material is synthesized in the charged state it does not enable Li to be brought into the Li-ion cell. The development of a high-performance Li-ion cathode based on the Mn$^{2+}$/Mn$^{4+}$ couple requires a material that forms in its discharged state, contains enough Mn$^{2+}$ and Li$^{+}$ ions to provide high capacity and preferably crystallizes in a dense structure, such as the layered or disordered-rocksalt structure, to maximize its volumetric energy density. Introducing Mn$^{2+}$ in the dense layered or disordered materials has been difficult, as the Li excess (x > 1 in Li$_x$TM$_{3−x}$O$_2$, where TM is transition metal) required to achieve high practical capacity$^{10,13,14}$ demands a high average transition metal valence.

In this work, we demonstrate that high capacity (>300 mAh g$^{-1}$) and energy density (about 1,000 Wh kg$^{-1}$) can be achieved in disordered-rocksalt Li-rich intercalation cathodes from Mn$^{2+}$/Mn$^{4+}$ double redox combined with a small amount of O redox. A critical step is that we are able to lower the Mn valence in the cathode material through a combined strategy of high-valent cation (Nb$^{5+}$, Ti$^{4+}$) substitution$^{15}$ and O$^{2−}$ replacement$^{16–18}$ by F$^{−}$. This O$^{2−}$ replacement was recently shown to be aided by Li excess and cation disorder$^{15}$. We target the Mn$^{2+}$-containing compositions Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F and Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F, which have a theoretical Mn$^{2+}$/Mn$^{4+}$ redox capacity of 270 mAh g$^{-1}$ and 230 mAh g$^{-1}$, respectively. Given the high Mn capacities, only a small amount of O redox is required for these materials to deliver a total capacity over 300 mAh g$^{-1}$, mitigating problems related to O redox. Thus realized, high capacity from Mn$^{2+}$/Mn$^{4+}$ double redox
opens new opportunities for the design of high-performance Li-ion cathode materials.

**Structural characterization of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F**

To evaluate the Mn$^{3+}$/Mn$^{4+}$ redox strategy, we first test a new disordered Li-rich material: Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F (equivalent to Li$_{1.33}$Mn$_{2.44}$Nb$_{0.22}$Os$_{0.66}$), synthesized by a mechanochemical ball-milling method$^{11,16,17}$. The combined presence of high-valent Nb$^{5+}$ and low-valent F$^-$ sets up the charge balance to incorporate Mn as Mn$^{2+}$ in the pristine Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F material, leading to a very high theoretical Mn-redox capacity of 270 mAh g$^{-1}$, which is more than twice that of a typical Mn-based Li-rich cathode material (Fig. 1a). In addition, the Nb$^{5+}$ configuration of Nb$^{5+}$ (similar to that of Ti$^{4+}$, V$^{5+}$, Zr$^{4+}$ and Mo$^{6+}$) promotes the formation of a disordered-rocksalt structure$^{18}$.

X-ray diffraction (XRD) patterns (Fig. 1b, Extended Data Table 1) and elemental analysis (Extended Data Table 2) show that the compound forms in a disordered-rocksalt phase with a composition close to the target composition$^{11}$. XRD refinement yields a lattice parameter of about 4.262 Å (Extended Data Table 1). Energy-dispersive spectroscopy mapping (EDS) on a Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F particle, using a transmission electron microscope (TEM), reveals a uniform distribution of Mn, Nb, O and F (Fig. 1c). Results of $^7$Li and $^{19}$F nuclear magnetic resonance (NMR) reveal that some Li can be found in diamagnetic environments and some F can be found in LiF-like environments (Extended Data Fig. 1, Methods section ‘Supplementary Note 1’). Although this suggests that small amounts of impurity phases (for example Li$_2$O, Li$_2$CO$_3$) may be present in the as-synthesized Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F sample, we cannot rule out the presence of diamagnetic or LiF-like local domains in the rocksalt phase. In fact, no crystalline impurities could be detected with XRD. TEM shows that the primary particles are polycrystalline and made of crystalline grains about 15 nm in size (Extended Data Fig. 2). No amorphous components were detected in TEM, indicating that the electrochemical properties are predominantly determined by the Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F phase. Scanning electron microscopy (SEM) shows that the primary particle size of the as-prepared Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F compound is 100–300 nm (Fig. 1d), which is reduced to less than 100 nm after mixing with carbon black using a shaker-mill for electrode fabrication (Fig. 1e).

**Electrochemical performance of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F**

Galvanostatic charge–discharge tests of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F at 20 mA g$^{-1}$ show a discharge capacity of 238 mAh g$^{-1}$ (708 Wh kg$^{-1}$) between 1.5 V and 4.6 V, which increases to 277 mAh g$^{-1}$ (849 Wh kg$^{-1}$) and 304 mAh g$^{-1}$ (945 Wh kg$^{-1}$) with higher charge cut-off voltages of 4.8 V and 5.0 V, respectively (Fig. 2a–c). In a test between 1.5 V and 5.0 V at 10 mA g$^{-1}$ (Fig. 2d), the discharge capacity further increases to 317 mAh g$^{-1}$, delivering a very high energy content of 995 Wh kg$^{-1}$ (3.761 Wh g$^{-1}$). This discharge capacity of about 320 mAh g$^{-1}$ and specific energy approaching 1,000 Wh kg$^{-1}$ are among the highest values achieved by Li-ion intercalation cathodes$^{10–12,19}$. The reversible capacity and energy density at 20 mA g$^{-1}$ decrease to 233 mAh g$^{-1}$ (180 mAh g$^{-1}$) and 760 Wh kg$^{-1}$ (600 Wh kg$^{-1}$), respectively, as the voltage window is reduced to 2.0–4.8 V (2.3–4.6 V) (Extended Data Fig. 3). The rate capability of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F is fairly good. Figure 2e compares the first cycle profile of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F under different rates between 1.5 V and 3.0 V. The material delivers as high as 226 mAh g$^{-1}$ (695 Wh kg$^{-1}$) at 200 mA g$^{-1}$ and up to 140 mAh g$^{-1}$ (410 Wh kg$^{-1}$) at a very high rate of 1,000 mA g$^{-1}$ (Extended Data Fig. 4). The data presented here were obtained on electrode films made of 60 wt% active material, but the performance is similar for electrodes with a higher loading of 70 wt% and 80 wt% (Extended Data Fig. 3).

The voltage profiles of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F do not contain significant hysteresis and remain nearly identical during cycling, suggesting that structural changes and oxygen loss are small$^{19,20,21}$. Only upon very high-voltage charging to above 4.7 V is an apparent voltage plateau observed which is barely seen in discharge (Fig. 2f). As Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F delivers a higher capacity than its theoretical Mn capacity (270 mAh g$^{-1}$), we expect that the charge plateau at about 4.8 V accompanies O-oxidation. The asymmetry in charge/discharge voltage is similar to previous observations in which the O-oxidation plateau is not recovered in the discharge$^{8,20,21}$. Nevertheless, this plateau in Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F appears only after charging above about 250 mAh g$^{-1}$, leading to less voltage hysteresis than for the other Mn-redox-active disordered compounds in which the O-oxidation plateau occurs typically much earlier in the charge$^{8,20,21}$. The smaller amount of O-oxidation and negligible changes in the voltage profile of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F are further supported by differential electrochemical mass spectrometry (DEMS) results, which show negligible O$_2$ (g) evolution up to a charge of 5 V (Extended Data Fig. 5, Methods section ‘Supplementary Note 2’). In addition, voltage fade is small in this material (Extended Data Fig. 6, Methods section ‘Supplementary Note 3’). These results indicate that our strategy of going to Mn$^{2+}$- compounds to increase the Mn-redox capacity at the expense of O redox is successful in increasing capacity and reversibility.

**Redox mechanism of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F**

The redox mechanism and structural evolution of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F have been further studied by X-ray diffraction, and by hard X-ray and X-ray absorption spectroscopy (XAS). The redox mechanism and structural evolution of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F have been further studied by X-ray diffraction, and by hard X-ray and X-ray absorption spectroscopy (XAS).
soft X-ray absorption spectroscopically. Figure 3a shows a reversible lattice-parameter change upon cycling, as observed in other disordered-rocksalt intercalation cathodes. The shift of the (002) and (022) peaks to a higher angle upon charge (indicating a decrease of lattice parameters) is recovered on discharge. Upon charging, the lattice parameter decreases from 4.258 Å to 4.130 Å at the top of charge and returns to 4.250 Å after full discharge.

Hard X-ray absorption spectroscopy (XAS) suggests that Mn²⁺ is oxidized during charge towards Mn⁴⁺, a process that is reversed upon discharge. Figure 3b shows the Mn K-edge X-ray absorption near-edge structure (XANES) for Li₂Mn₂/₃Nb¹/₃O₂F at various states of charge and discharge. As the charge capacity increases from 0 to 135 mAh g⁻¹ and 270 mAh g⁻¹, the Mn K-edge shifts from an energy close to MnO (Mn²⁺ reference) to that of Mn₂O₃ (Mn³⁺ reference) and then partway to the energy seen in MnO₂ (Mn⁴⁺ reference). Further charging to 360 mAh g⁻¹ leads to only minor shifts. The Mn K-edge almost completely returns to its original position after discharge. Although the exact amount of each valence state cannot be quantified, as the near-edge structure is sensitive to both the oxidation state and bonding environment, this result suggests that, on full charge, Mn²⁺ is oxidized to Mn³⁺ with some Mn³⁺ or Mn⁴⁺ ions remaining. Full recovery to Mn²⁺ occurs on discharge. This interpretation is further supported by a derivative analysis on the Mn pre-edge at about 6,540 eV (Extended Data Fig. 7, Methods section).

Fig. 2 | Electrochemical performance of Li₂Mn₂/₃Nb¹/₃O₂F. a–d, Voltage profiles and capacity retention of Li₂Mn₂/₃Nb¹/₃O₂F under various cycling conditions: a, 1.5–4.6 V, 20 mA g⁻¹; b, 1.5–4.8 V, 20 mA g⁻¹; c, 1.5–5.0 V, 20 mA g⁻¹; and d, 1.5–5.0 V, 10 mA g⁻¹. e, The first-cycle voltage profiles of Li₂Mn₂/₃Nb¹/₃O₂F when cycled between 1.5 V and 5.0 V at 10, 20, 40, 100, 200, 400 and 1,000 mA g⁻¹. f, The first-cycle and second-charge profiles of Li₂Mn₂/₃Nb¹/₃O₂F under different voltage windows: 1.5–4.6 V, 1.5–4.8 V and 1.5–5.0 V. All tests were conducted at room temperature.

Fig. 3 | Reaction mechanism of Li₂Mn₂/₃Nb¹/₃O₂F. a, XRD patterns of Li₂Mn₂/₃Nb¹/₃O₂F during the first cycle at 10 mA g⁻¹ and the refined a-lattice parameters (c, charge; dc, discharge). b, c, Manganese K-edge XANES spectra from hard XAS (b) and O K-edge spectra from soft XAS (c; using total fluorescence yield mode) during the initial cycle. Features A and B are described in the text. Plots are shown for Li₂Mn₂/₃Nb¹/₃O₂F before cycling: 135 mAh g⁻¹ charged; 270 mAh g⁻¹ charged; 360 mAh g⁻¹ charged; 320 mAh g⁻¹ discharged after a 375 mAh g⁻¹ charge.
pre-edge shape and intensity, indicating Mn and O reduction. Hence, the electrochemical processes in this compound are reversible.

**Ab initio study of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F**

In conventional Li–Mn oxides (for example LiMnO$_2$, Li$_2$MnO$_3$), Mn oxidation up to Mn$^{3+}$ is not competitive with O oxidation$^{8,10,20,21}$. The question is then why there is a partial overlap between these redox processes in Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F. The main differences between Li$_2$Mn$_2$NbO$_4$F and other Mn-based Li-excess oxides are the presence of fluorine and the relatively large lattice parameter ($a$ is about 4.26 Å for Li$_2$Mn$_2$NbO$_4$F compared with about 4.19 Å for Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F), which leads to a larger distance between Mn and the ligand. To elucidate the impact of these features on electrochemical behaviour, we study the effect of F-coordination and lattice volume on the redox mechanism using density functional theory calculations. Note that although we compute the redox mechanism through electron titration as described in the Methods section, for clarity we refer to the degree of charge in terms of Li content.

Figure 4a, b shows the Mn and O average oxidation states as a function of delithiation ($x$ in Li$_2$-$x$Mn$_{2/3}$Nb$_{1/3}$O$_2$F) and for varying degrees of compressive strain relative to the fully relaxed discharged state ($x = 0$). c, Change in the average oxidation state of Mn atoms that are coordinated by three or more fluorine atoms and those coordinated by two or fewer fluorine atoms. d, Change in the average oxidation state of O atoms with three, four and five Li nearest neighbours in the fully lithiated state ($x = 0$). The data in c and d were collected from model structures without strain and are representative of trends seen at all levels of strain. The expected average oxidation state given in c–d is sampled from 12 representative structural models of disordered-rocksalt Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F, with an error bar equal to the standard deviation of this value. e, A schematic band structure of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F.

**Structure and performance of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F**

With diverse choices of high valent cations, Mn$^{2+}$/Mn$^{4+}$ double redox can be realized in many different systems. As a demonstration, we have developed another new material, Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F, in which Ti$^{4+}$ is the high-valent cationic species. This material also forms a disordered-rocksalt phase ($a = 4.206$ Å), as can be inferred from the XRD pattern in Fig. 5a (Extended Data Table 1). SEM shows that, after mixing the compound with carbon black using a shaker-mill, the average primary particle size is about 50 nm (Fig. 5b). TEM-EDS shows a uniform distribution of Mn, Ti, O and F (Fig. 5c). As in the case of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F, the primary particles of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F are polycrystalline and made of grains about 15 nm across (Extended Data Fig. 1). However, the presence of Mn–F bonds, the Li-excess O environments and the larger bond distance of Mn–O(F) in this material all contribute to some competitive Mn/O oxidation at very high states of charge (Fig. 5e). Nevertheless, owing to the large Mn$^{2+}$/Mn$^{4+}$ reservoir, O redox is much less needed in Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F than in other Mn-based Li-rich materials, rendering Mn double redox an effective way to achieve high capacity without the typical polarization and capacity fade that is observed with excessive use of the oxygen redox.
among the highest values achieved by advanced cathode materials. Additional electrochemical data (rate tests, voltage window tests, change of the electrode formulation) are presented and discussed in Extended Data Fig. 10 and Methods section ‘Supplementary Note 5’.

As in Li₂Mn₂/₃Nb₁/₃O₂F, the voltage profiles of Li₂Mn₁/₂Ti₁/₂O₂F barely change after the first cycle, indicating a reversible reaction without a major structural change or O loss, as evidenced by the DEMS results (Extended Data Fig. 5). The O-oxidation plateau appears only after charging above 230 mA g⁻¹ (above about 4.6 V), which is substantially delayed compared with other Mn-based Li-rich materials. Nevertheless, this plateau is slightly longer than in Li₂Mn₂/₃Nb₁/₃O₂F, probably owing to the smaller Mn²⁺ content in Li₂Mn₁/₂Ti₁/₂O₂F, requiring more O oxidation to achieve a given capacity.

Ex situ XRD of Li₂Mn₁/₂Ti₁/₂O₂F indicates a reversible change in lattice parameter, shrinking from about 4.203 Å to about 4.105 Å after a 400 mA g⁻¹ charge and then recovering to about 4.194 Å after a 330 mA g⁻¹ discharge (Fig. 5f). Hard XAS confirms Mn²⁺/Mn⁴⁺ redox in the material (Extended Data Fig. 11, Methods section ‘Supplementary Note 6’). As in Li₂Mn₂/₃Nb₁/₃O₂F, additional capacity beyond Mn-redox capacity is probably delivered by O redox. Based on its high capacity and reversibility, Li₂Mn₁/₂Ti₁/₂O₂F has considerable potential as a high-performance Li-ion cathode.

**Outlook for Mn²⁺/Mn⁴⁺ redox**

Double redox couples are tremendously important for the development of advanced cathodes. Indeed, today’s modern NMC-based layered cathodes all rely to some extent on the Ni²⁺/Ni⁴⁺ double redox. With Li₂Mn₂/₃Nb₁/₃O₂F and Li₂Mn₁/₂Ti₁/₂O₂F, we have demonstrated that combined fluorination and high-valent cation substitution can introduce Mn²⁺/Mn⁴⁺ redox in a Li-excess disordered-rocksalt structure, which leads to high-capacity Mn-based Li-excess cathodes (capacity of >300 mA h g⁻¹, energy density of around 1000 Wh kg⁻¹) without an excessive use of O redox. This discovery is important, as our strategy can be widely applied to design high-performance Mn-based Li-excess cathodes that do not suffer from structural degradation triggered by extensive O redox.

The combination of Mn²⁺/Mn⁴⁺ redox with the cation-disordered structure and the partial replacement of O by F leads to a large chemical space for new cathode materials. We expect to see considerable optimization through the use of different high-valent charge-compensating elements, as well as through minor alloying additions to stabilize the structure further and increase other performance aspects. The disordered-rocksalt framework has previously shown high structural stability and compositional flexibility, enabling by not requiring the preservation of the layered cathode structure, which can be used to tune not only the Li-excess level for Li transport but also the content of F and high-valent cations (such as Sn⁴⁺, Sb⁵⁺, and Te⁶⁺). These handles can all be used to modify the size of the Mn²⁺/Mn⁴⁺ reservoir and balance Mn- and O-redox activities. Critical directions for further research include finding ways of decreasing the voltage slope of these compounds, so that their high capacity and energy density can be delivered over a narrower voltage window, as well as investigating Mn dissolution which often underlines the long-term cyclability of Mn-based cathodes. Strategies based on compositional modifications of the cathode material, on changes in the short-range cation distribution, or on microstructure control (for example by surface coating) and on the use of tailored electrolytes should be explored to further develop high-performance Mn²⁺/Mn⁴⁺-based cathodes for advanced Li-ion batteries.

**Online content**

Any Methods, including any statements of data availability and Nature Research reporting summaries, along with any additional references and Source Data files, are available in the online version of the paper at [https://doi.org/10.1038/s41586-018-0015-4](https://doi.org/10.1038/s41586-018-0015-4).

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Author contributions J.L. and G.C. planned the project. G.C. supervised all aspects of the research. J.L. designed, synthesized, characterized (XRD) and electrochemically tested the proposed compounds. D.A.K. performed density functional theory calculations and analysed the data with J.L. D.-H.K. acquired and analysed TEM data. C.-W.L. and M.B. acquired and analysed hard XAS data. J.K.P. acquired and analysed SEM data with input from B.D.M., Y.-S.L. and J.G. performed soft XAS measurements and analysed the data with J.L. Z.L. performed supportive electrochemical measurements. R.J.C. acquired and analysed the NMR data. T.S. performed SEM. The manuscript was written by J.L. and G.C. and was revised by D.A.K. and R.J.C. with the help of the other authors. All authors contributed to discussions.

Competing interests The authors declare no competing interests.

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METHODS

Synthesis. To synthesize Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F$_x$, we used Li$_2$O (Sigma-Aldrich, 97%), MnO (Alfa Aesar, 99%), Nb$_2$O$_5$ (Alfa Aesar, 99.9%) and LiF (Alfa Aesar, 99.9%) as precursors. For Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F$_x$ we used Li$_2$O (Sigma-Aldrich, 97%), MnO (Alfa Aesar, 99%), TiO$_2$ (Alfa Aesar, 99.9%) and LiF (Alfa Aesar, 99.9%) as precursors. Other than Li$_2$O, for which we used 10% excess (rather than stoichiometric amount) to compensate for possible loss of Li$_2$O during synthesis, stoichiometric amounts of precursors were dispersed into an Ar-filled stainless steel jars and then the planetary ball-milled (Retch PM 200) for 40 h at the rate of 450 r.p.m., during which Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F or Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F form mechanochemically. The total amount of precursors in each jar (50 mL) was approximately 1 g, and five 10-mm-diameter and ten 5-mm-diameter stainless balls were used as the grinding media.

Electrochemistry. To prepare a cathode film from Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F or Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F, 480 mg of active compounds and 240 mg of carbon black (Timcal, SUPER C65) were first mixed for an hour in an Ar-filled 45-mL zirconia vial with 10 g of 5-mm-diameter yttria-stabilized zirconia balls (Inframat Advanced Materials) as grinding media, using a SPEX 8000M Mixer/Mill. Polytetrafluoroethylene (PTFE, DuPont, Teflon 8A) was then added to the mixture as a binder, such that the cathode film consists of the active compounds, carbon black and PTFE in the weight ratio of 60:30:10. The weight ratio for cathode films with higher active-material loading was either 70:20:10 or 80:15:5. The components were then manually mixed using a mortar and pestle and rolled into a thin film inside an Ar-filled glove box. To assemble a cell for all cycling tests, 1 M of LiPF$_6$ in ethylene carbonate and dimethyl carbonate (EC/DMC) solution (1:1, RASF), glass microfibre filters (Whatman) and Li metal foil (FMC) were used as the electrolyte, the separator and the counter electrode, respectively. The cells were assembled in an Ar-filled glove box and tested on a Maccor 2200 or an Arbin battery cycler at room temperature in the galvanostatic mode. The loading density of the cathode film was about 6 mg cm$^{-2}$.

The redox mechanism was performed with the Vienna Ab-Initio Simulation Package (VASP) using the projector augmented-wave method. First, structural models of the Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F ordered rocksalt were obtained using a cluster-expansion-based Monte Carlo simulation, chosen to find low-energy disordered structures with representative short-range order, while suppressing phase separation. The cluster-expansion Hamiltonian used for the Monte Carlo simulations consists of a decomposition of the internal energy of a particular atomic configuration on a rocksalt lattice into contributions from two- , three- and four-body terms up to maximum interaction distance of 7 Å, 4 Å and 4 Å respectively, and five-body terms up to maximum interaction distance of 10 Å, on top of an electrostatic model based on the formal charges of all species. To obtain the interaction terms, we first calculated 450 representative configurations of Li$^{1+}$, Mn$^{2+}$, Nb$^{5+}$, O$^{2-}$ and F$^{-}$ on a rocksalt lattice within the Perdew–Burke–Ernzerhof exchange-correlation functional, supplemented with the rotationally invariant Hubbard $U$ correction to the transition metal $d$ states to correct self-interaction error ($U_{	ext{Hubb}} = 3.9$ eV, $U_{	ext{eff}} = 1.5$ eV based on previously reported fits to oxide for- mation enthalpies). These calculations were performed with a reciprocal-space discretization of 25 Å$^{-1}$, 520 eV plane-wave cut-off, and a 0.002 Å$^{-1}$ convergence on total energy and interatomic forces respectively. The strength of each cluster interaction, as well as the dielectric constant, was then fitted using a L$_1$-regularized least-squares regression, optimized by cross-validation, which resulted in an out-of-sample error of 0.04 eV per atom.

The redox mechanism of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F was calculated on 12 structural models of 36 atoms each, obtained from the Monte Carlo simulations described above. Oxidation calculations were done using the hybrid Heyd–Scuseria–Ernzerhof functional, using a 650 eV plane-wave cut-off, 10 Å$^{-1}$ reciprocal-space discretization, and a 0.002 eV and 0.002 Å$^{-1}$ convergence on total energy and interatomic forces respectively. The fraction of exact exchange was set to 0.30 on the basis of a calibration to the Kohn– Sham gaps of α-Mn$_2$O$_3$, α-MnOOH and β-MnO$_2$ calculated within the G$_{0}$W$_0$ approximation, following previously reported methodology for reproducing the redox competition between transition metals and oxygen. To investigate the order in which various redox couples are activated in the material, suppressing major structural rearrangements, we trace the oxidation state of each species (obtained from the magnetic moment of each atom) as electrons are removed from the material and charge compensated by a uniform background charge, allowing the local atomic arrangements to relax at each step using the LS-Dyna lattice frozen model. The order of oxidation reactions is determined by the character of the valence-band edge at various states of charge, such electron titration provides an efficient way to look at the electronic contribution to the redox mechanism.

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Supplementary Note 1. The absence of peaks other than those corresponding to the disordered-rolls phase spectra in the XRD data collected on as-synthesized Li2Mn2/3Nb1/3O2F and Li2Mn2/3Nb1/3O2F suggests that the samples are fairly phase-pure without large amounts of crystalline impurities such as LiF, LiO, or Li2O. Nevertheless, because small amounts of impurity phases or amorphous phases can be invisible to XRD, we investigated further using 1H and 19F NMR spectroscopy. 1H spin echo NMR spectra, obtained on as-synthesized Li2Mn2/3Nb1/3O2F and Li2Mn1/2Ti1/2O2F samples, are shown in Extended Data Fig. 1a, b. The data have been fitted using a minimum of three Li sites: Li1, Li2 and Li3. The fits suggest about 78%–79% ±2% of Li in paramagnetic environments (Li1 and Li2 signals), and about 21%–22% ±2% Li in diamagnetic environments (Li3 signal). The broad Li1 and Li2 resonances are ascribed to several paramagnetic Li environments close to open-shell Mn and with very similar shifts, resulting in overlapping signals. Paramagnetic interactions between unpaired Mn 7/2 electrons and the Li nuclei lead to a broadening of the individual Li signals with shifts centred around 64.9 ppm (Li1) and −27.4 ppm (Li2) for Li2Mn2/3Nb1/3O2F; and around 57.7 ppm (Li1) and −25.5 ppm (Li2) for Li2Mn1/2Ti1/2O2F. The sharper Li3 resonance, with a shift close to 0 ppm (−0.1 ppm for Li2Mn2/3Nb1/3O2F and −0.5 ppm for Li2Mn1/2Ti1/2O2F), is assigned to diamagnetic Li sites in the samples. Because Li1, Ni+ and Ti4+ do not have unpaired electrons, Li nuclei in diamagnetic Li/Ti- and Li/Nb-rich domains in Li2Mn2/3Nb1/3O2F and Li2Mn1/2Ti1/2O2F have a shift around 0 ppm that cannot be distinguished from that of potential LiO, LiF and Li2CO3 impurities, resonating at 2.8, −1 and 0 ppm, respectively51. All of these Li environments may contribute to the Li3 signal, and individual contributions cannot be quantified. In fact, local segregation of cations that would lead to Li environments in different local domains is observed in several compounds—for example, Li2Mn2/3O2-like domains in Li- and Mn-rich layered Ni–Mn–Co materials40, or Li/NbO2-like local domains in disordered Li–V–Nb–O materials41. A previous 1H NMR study on paramagnetic Li transition metal phosphates (LiMPO4) cathodes has found that paramagnetic shift contributions from distant Mn beyond the second metal coordination shell around the central Li can be non-zero51. This observation suggests that, in Li2Mn2/3Nb1/3O2F and Li2Mn1/2Ti1/2O2F, Mn is likely to be more than 7 Å away from the Li for there to be no paramagnetic shift contribution and an overall Li shift close to 0 ppm.

1H spin echo sum spectra, collected on as-synthesized Li2Mn2/3Nb1/3O2F and Li2Mn1/2Ti1/2O2F, are compared to the spin echo spectrum collected on crystalline LiF powder and presented in the Extended Data Fig. 1c. Further details on how the sum spectra were obtained can be found in the Methods section for solid state NMR spectroscopy where we describe the method of ‘spin echo mapping’. The 19F NMR data clearly indicate that most of the F is found in paramagnetic environments (that is, with Mn in the first, second and/or third metal coordination shell around the F nucleus), giving rise to very broad overlapping NMR signals shifted away from the LiF resonant frequency. Nevertheless, LiF-like F environments are also observed in our spectra with a resonant frequency equal to that of pure LiF (−204 ppm). Some of our current work on similar paramagnetic cation-disordered oxyfluorides suggests that F nuclei directly bonded to the paramagnetic centre (here Mn) are essentially invisible in the NMR spectrum, because the very strong interaction with the unpaired electrons leads to extremely broad resonances with a very large shift that are lost in the background. Hence, we suspect our 19F NMR data not to be quantitative and the proportion of F in paramagnetic environments to be even larger than that determined from experimental observations. With this in mind, the 19F NMR data confirm that most of the F has integrated into the bulk cation–disordered oxide lattice. Although the −204 ppm 19F signal can indicate LiF impurity in our samples, it can also indicate the presence of a small proportion of LiF-like domains in the disordered oxyfluoride structure, which would be consistent with recent theory work59 showing that the much higher energetic cost of creating M–F bonds, as compared with Li–F bonds, results in the incorporation of F in Li-rich (that is, LiF-like) local environments in cation-disordered oxyfluoride materials.

In short, diamagnetic Li sites and LiF-like F environments observed with NMR cannot be uniquely attributed to either local domains in the rocksalt structure or to amorphous impurity phases, such as LiF, LiO or Li2O, in our samples. Hence, NMR can give us an upper bound to the amount of impurity present in the samples but does not enable us to obtain the exact amount of potential impurity phases. In the extreme case in which all of the diamagnetic Li and LiF-like F signals come from LiO and LiF, the total weight fraction of impurity phases is estimated to be no more than 6–7 wt%; it is likely to be less, as no crystalline impurities were observed with XRD and no amorphous domains were observed in TEM (Extended Data Figs. 2, 9). As a result, we are confident stating that the performance of Li2Mn2/3Nb1/3O2F and Li2Mn2/3Nb1/3O2F is predominantly determined by the transition metal cation state to mass ratios allowed in the non-centrosymmetric environment. Direct comparison of the Mn K-edge pre-edge features of Li2Mn2/3Nb1/3O2F upon cycling is shown in Extended Data Fig. 7b. To analyse their shape more clearly, first derivatives of their pre-edges are
shown in Extended Data Fig. 7c–e. The first derivatives of the spectra from ‘before cycle’ and ‘after first charging to 375 mAh g⁻¹ then discharging to 320 mAh g⁻¹’ resemble that of MnO (Extended Data Fig. 7c), suggesting that most Mn ions in the two samples are in the Mn²⁺ state. After first charging Li₂Mn₂/3Nb₁/3O₂F to 135 mAh g⁻¹, the derivative shape looks similar to that of MnO₂, indicating the presence of Mn⁴⁺ in the sample (Extended Data Fig. 7d). After charging to 270 and 360 mAh g⁻¹, the derivative shape changes towards that of MnO₂, indicating mostly Mn⁴⁺ ions although Mn²⁺ and Mn⁵⁺ might also be present (Extended Data Fig. 7e).

Supplementary Note 5. Li₂Mn₁/2Ti₁/2O₂F exhibiting cycling behaviour, as does Li₂Mn₂/3Nb₁/3O₂F. When cycled between 1.6 V and 5.0 V (Extended Data Fig. 10a), 2.0 V and 4.8 V (Extended Data Fig. 10b), and 2.3 V and 4.6 V (Extended Data Fig. 10c) at 20 mA g⁻¹, the 60 wt%:30 wt%:10 wt% = Li₂Mn₁/2Ti₁/2O₂F: carbon black:PTFE electrode delivers discharge capacities up to 306 mAh g⁻¹ (920 Wh kg⁻¹), 227 mAh g⁻¹ (739 Wh kg⁻¹), and 160 mAh g⁻¹ (534 Wh kg⁻¹), respectively. Rate capability of Li₂Mn₁/2Ti₁/2O₂F is acceptable. When cycled at high rates of 200 and 400 mA g⁻¹ between 1.6 V and 5.0 V, the material still delivers discharge capacities up to 210 mAh g⁻¹ (629 Wh kg⁻¹) and 158 mAh g⁻¹ (461 Wh kg⁻¹) (Extended Data Fig. 10d). Capacity retention of Li₂Mn₁/2Ti₁/2O₂F (Extended Data Fig. 7e) is good and is slightly better than that of Li₂Mn₂/3Nb₁/3O₂F (Extended Data Fig. 4). When cycled at 100 mA g⁻¹ and above, the capacity loss during initial 25 cycles is less than 0.4% per cycle. The 80 wt%:15 wt%:5 wt% = Li₂Mn₁/2Ti₁/2O₂F:carbon black:PTFE electrode exhibits similar performance to the 60 wt%:30 wt%:10 wt% = Li₂Mn₁/2Ti₁/2O₂F:carbon black:PTFE electrode (Extended Data Fig. 10b, f).

Supplementary Note 6. Extended Data Fig. 11a, b shows the Mn K-edge XANES spectra of Li₂Mn₁/2Ti₁/2O₂F before cycle, after charging to 120 mA h g⁻¹, 240 mA h g⁻¹ and 400 mA h g⁻¹, and after charging to 400 mA h g⁻¹ then discharging to 330 mA h g⁻¹. Upon first charging from 0 to 120 mA h g⁻¹ and 240 mA h g⁻¹, the Mn rising-edge shifts, from an energy in between those in MnO and MnO₂, to an energy in MnO₂ and then partway up to an energy in MnO. Further charge is small upon charging to 400 mA h g⁻¹. The edge returns to the original position after discharging to 330 mA h g⁻¹. This result suggests that Mn ions in the as-prepared Li₂Mn₁/2Ti₁/2O₂F compounds are mostly Mn²⁺ (possibly with some Mn³⁺), which are oxidized in charge towards Mn⁴⁺ with some Mn ions not fully oxidized. Upon discharge, Mn ions return to Mn²⁺. Note that because the shape of Mn K-edge spectra for a given oxidation state can vary a lot depending on bonding environment and there are no reported references for Mn-based disordered-oxyfluoride compounds, quantitative analysis of our results is difficult.

Derivative analysis on the Mn pre-edge feature at about 6.539 eV (Extended Data Fig. 11c–e) suggests the same Mn–redox mechanism. The first derivatives of the spectra from ‘before cycle’ and ‘after first charging to 400 mA h g⁻¹ then discharging to 330 mA h g⁻¹’ exhibit a mixed shape of the first-derivative spectra of MnO and MnO₂ (Extended Data Fig. 11d). This suggests an existence of Mn²⁺ ions with some partly oxidized Mn ions such as Mn³⁺. After first charging to 120 mA h g⁻¹, the derivative shape looks similar to that of MnO₂, indicating Mn³⁺ in the sample (Extended Data Fig. 11d). After charging to 240 and 400 mA h g⁻¹, the derivative shape changes towards that of MnO₂, suggesting a large amount of Mn⁴⁺ ions, but Mn²⁺ and Mn⁵⁺ might also be present (Extended Data Fig. 11e).

The Ti K-edge spectra of the Li₂Mn₁/2Ti₁/2O₂F samples (Extended Data Fig. 11f) resemble that of TiO₂ (Ti⁴⁺) and their rising-edge position barely changes during cycling, although there are minor changes in shape, which indicates local Ti-site distortion. This suggests that Ti exists as Ti⁴⁺ and is redox silent. Because Ti⁴⁺ is redox in active, we expect that reversible capacities of Li₂Mn₁/2Ti₁/2O₂F beyond Mn capacities come from O redox, as in the case of Li₂Mn₂/3Nb₁/3O₂F.

Data availability. The datasets generated and analysed during this study are available from the corresponding authors on reasonable request.
Extended Data Fig. 1 | Solid-state NMR spectroscopy results. a, b, $^7$Li spin echo NMR spectra acquired on as-synthesized Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F (a) and Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F (b) powders at 50 kHz MAS at a field $B_0 = 11.7$ T. The data have been fitted with a minimal number of Li sites: Li1, Li2 and Li3. Spinning sidebands of the three Li signals are indicated with asterisks. c, $^{19}$F spin echo sum spectra acquired on as-synthesized Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F and Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F powders at 50 kHz MAS at a field $B_0 = 11.7$ T. The spectra are compared to the spin echo spectrum collected on LiF under similar conditions. Spinning sidebands of the sharp LiF-like signals are indicated with asterisks. Detailed explanations of the results are given in Methods section ‘Supplementary Note 1’.
Extended Data Fig. 2 | Structural characterization of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F.

a, TEM image of as-synthesized Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F particles. Scale bar, 50 nm. b, A high-magnification TEM image of the area enclosed in a square in a. Scale bar, 10 nm. The yellow circle indicates the boundary of one of the many grains in the polycrystalline Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F particle.

c, An electron diffraction pattern of the Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F particle.

d, Fast Fourier-transformed (FFT) images of the dotted squared areas in b. e, The high magnification image across the squared areas 1, 2 and 3 in b. Scale bar, 5 nm. We can clearly observe lattice fringes and FFT peaks throughout the particle, indicating that our particles are made of small crystalline grains instead of amorphous phases.
Extended Data Fig. 3 | Additional electrochemical data from Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F. a, b, Voltage profiles of the 60:30:10 electrode (that is, 60 wt% Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F: 30 wt% carbon black: 10 wt% PTFE) when cycled between 2.0 V and 4.8 V (a), and 2.3 V and 4.6 V (b) at 20 mA g$^{-1}$.

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Extended Data Fig. 4 | Discharge capacity retention. The 60:30:10 Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$:F:carbon black:PTFE electrode was cycled between 1.5 V and 5.0 V at room temperature at 10, 20, 40, 100, 200, 400 and 1,000 mA g$^{-1}$. A faster rate leads to less capacity fading during the initial 25 cycles. This is likely to be due to electrolyte decomposition per cycle occurring more (less) at a high voltage in a slower (faster) cycling test, which increases the impedance of a cell by creating a resistive surface layer and decreasing the ionic conductivity of the electrolyte.
Extended Data Fig. 5 | Gas evolution measurements. a, b, Initial voltage profiles (black solid line) of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F (a) and Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F (b), when charged to 5.0 V at a rate of 20 mA g$^{-1}$. DEMS results for O$_2$ (red circles) and CO$_2$ (blue triangles) evolution are also shown. c, Cumulative CO$_2$ evolution from shaker-mixed Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F and carbon black powder mixture, as a function of time during an acid titration test using 1 M H$_2$SO$_4$. Detailed explanations of the results are given in Methods section ‘Supplementary Note 2’. 1st c, first charge.
Extended Data Fig. 6 | Evolution of the charge and discharge voltages. Average charge voltage (triangles), discharge voltage (stars), and half of the charge–discharge voltage (circles) are shown when Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F is cycled between 1.5 V and 4.6 V, 1.5 V and 4.8 V, and 1.5 V and 5.0 V, at 20 mA g$^{-1}$. Detailed explanations of the results are given in Methods section ‘Supplementary Note 3’. c, charge; dc, discharge.
Extended Data Fig. 7 | XANES of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F.  

(a, b) Manganese K-edge XANES spectra of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F: before cycle, after first charging to 135 mAh g$^{-1}$, 270 mAh g$^{-1}$ and 360 mAh g$^{-1}$, and after first charging to 375 mAh g$^{-1}$ then discharging to 320 mAh g$^{-1}$.

c–e, First derivatives of normalized absorbance at the pre-edge region of Mn K-edge spectra of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F: (c) before cycle and after first charging to 375 mAh g$^{-1}$ then discharging to 320 mAh g$^{-1}$; (d) after first charging to 135 mAh g$^{-1}$; and (e) to 270 mAh g$^{-1}$ and 360 mAh g$^{-1}$. Data from MnO, Mn$_2$O$_3$ and MnO$_2$ are presented for comparison. Detailed explanations of the results are given in Methods section ‘Supplementary Note 4’.
Extended Data Fig. 8 | Niobium K-edge XANES spectra of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F obtained by hard XAS. Results are shown before cycle, after charging to 135 mAh g$^{-1}$, 270 mAh g$^{-1}$ and 360 mAh g$^{-1}$, and after charging to 375 mAh g$^{-1}$ then discharging to 320 mAh g$^{-1}$. The Nb K-edge XANES spectra of the Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F samples are similar to that of Nb$_2$O$_5$ (Nb$^{5+}$ reference), indicating that Nb in the compound stays as Nb$^{5+}$ during cycling. The observable small shape changes are likely to be related to changes in local disorder and distortion$^{60}$. © 2018 Macmillan Publishers Limited, part of Springer Nature. All rights reserved.
Extended Data Fig. 9 | Structural characterization of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F.

a, TEM image of as-synthesized Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F particles. Scale bar, 50 nm.
b, A high-magnification TEM image of the area enclosed in a square in a. Scale bar, 10 nm. The yellow circle indicates the boundary of one of the many grains in the polycrystalline Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F particle.
c, An electron diffraction pattern of the Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F particle. Scale bar, 5 nm$^{-1}$.
d, FFT images of the dotted squared areas in b. e, The high-magnification image across the squared areas 1, 2 and 3 in b. Scale bar, 5 nm. We can clearly observe lattice fringes and FFT peaks throughout the particle, indicating that our particles are made of small crystalline grains instead of amorphous phases.
Extended Data Fig. 10 | Electrochemical properties of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F.

**a–c,** Voltage profiles and capacity retention of the 60:30:10 Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$:carbon black:PTFE electrode when cycled at 20 mA g$^{-1}$ at room temperature between 1.6 V and 5.0 V (**a**), 2.0 V and 4.8 V (**b**), and 2.3 V and 4.6 V (**c**). **d,** The initial charge–discharge profile of the 60:30:10 electrode when cycled between 1.6 V and 5.0 V at room temperature at 20, 40, 100, 200, 400 and 1,000 mA g$^{-1}$. **e,** The discharge capacities during initial 25 cycles. **f,** Voltage profiles and capacity retention of the 80:15:5 electrode when cycled at 20 mA g$^{-1}$ at room temperature between 2.0 V and 4.8 V. The specific capacity was calculated on the amount of the Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F powder in the cathode film. Detailed explanations of the results are given in Methods section ‘Supplementary Note 5’.
Extended Data Fig. 11 | XANES of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F. a, b, Manganese K-edge XANES spectra of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F: before cycle (black), 120 mAh g$^{-1}$ charged (navy), 240 mAh g$^{-1}$ charged (wine), 400 mAh g$^{-1}$ charged (grey), 330 mAh g$^{-1}$ discharged after a 400 mAh g$^{-1}$ charge (dark yellow). c–e, First derivatives of normalized absorbance at the pre-edge region of Mn K-edge spectra of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F: c, before cycle and after first charging to 400 mAh g$^{-1}$ then discharging to 330 mAh g$^{-1}$; d, after first charging to 120 mAh g$^{-1}$; and e, to 240 mAh g$^{-1}$ and 400 mAh g$^{-1}$. f, Titanium K-edge XANES spectra of Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F during the initial cycle. Data from MnO, Mn$_2$O$_3$, MnO$_2$, Ti$_2$O$_3$ and TiO$_2$ are presented for comparison. Detailed explanations of the results are given in Methods section ‘Supplementary Note 6’.
Extended Data Table 1 | Structural parameters from the Rietveld refinements

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<th>Materials</th>
<th>Li$<em>2$Mn$</em>{2/3}$Nb$_{1/3}$O$_2$F</th>
<th>Li$<em>2$Mn$</em>{1/2}$Ti$_{1/2}$O$_2$F</th>
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<tr>
<td>Mn occupancy</td>
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</tr>
<tr>
<td>Ti occupancy</td>
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<td>Volume (Å$^3$)</td>
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<tr>
<td>Derived density (kg/l)</td>
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The Rietveld refinements are shown in Figs. 1b and 5a. The crystallographic information file of Fm-3m LiFeO$_2$ (ICSD collection code 51208) was used as an input file. A pseudo-Voigt fit was used ($U/W = 8.0691, -0.9697, 1.3778$ for Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F, and $5.8736, -1, 1.4118$ for Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F). The atomic occupancies were initially set to the atomic ratio obtained from elemental analysis by direct-current plasma emission spectroscopy and an ion-selective electrode, based on which the lattice parameters were first refined. We then further refined the lattice parameters and the atomic occupancies together. Transition-metal occupancies were first refined freely. Then O and F occupancies were individually refined with a constraint of their occupancies summing to 1. Finally, all atomic occupancies including Li occupancy were simultaneously refined with the additional constraint that the total transition-metal occupancy should stay unchanged during this final process. However, as O and F are difficult to distinguish by XRD, and Li cannot be seen clearly, their occupancy values are more subject to error.
### Extended Data Table 2 | Target versus measured atomic ratio of Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F and Li$_2$Mn$_{1/2}$Ti$_{1/2}$O$_2$F compounds

<table>
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<tr>
<th>Materials</th>
<th>Li$<em>2$Mn$</em>{2/3}$Nb$_{1/3}$O$_2$F (Li : Mn : Nb : F)</th>
<th>Li$<em>2$Mn$</em>{1/2}$Ti$_{1/2}$O$_2$F (Li : Mn : Ti : F)</th>
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<tbody>
<tr>
<td>Target atomic ratio</td>
<td>2 : 0.666 : 0.333 : 1</td>
<td>2 : 0.5 : 0.5 : 1</td>
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<tr>
<td>Measured atomic ratio</td>
<td>1.852 : 0.660 : 0.333 : 1.05</td>
<td>2.01 : 0.514 : 0.475 : 1.05</td>
</tr>
</tbody>
</table>

Measurements were made by direct-current plasma emission spectroscopy (Li, Mn, Nb, Ti) and with an ion-selective electrode (F).