High capacity manganese layered-perovskite cathode for fluoride ion batteries involving cationic and anionic redox reaction

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Abstract

Developing electrochemical high-energy storage systems is of crucial importance towards a green and sustainable energy supply. A promising candidate is fluoride ion batteries (FIBs), which can deliver a higher energy density than is possible with lithium ion batteries\textsuperscript{1,2}. However, conversion-type reactions with metal fluorides causes a poor electrochemical reversibility\textsuperscript{1,3,4}. Recently, layered perovskite oxides such as LaSrMnO\textsubscript{4} have been shown to undergo topotactic electrochemical (de)fluorination, but they have low reversible discharge capacities (25 ~ 100 mAh/g) and poor rate capabilities. Here we show that a double-layered perovskite oxyfluoride La\textsubscript{1.2}Sr\textsubscript{1.8}Mn\textsubscript{2}O\textsubscript{7}–xF\textsubscript{2} exhibits topotactic (de)intercalation reaction inside the rock-salt slabs, achieving a large reversible capacity of 535 mAh/cm\textsuperscript{3} (0 ≤ x ≤ 2 in La\textsubscript{1.2}Sr\textsubscript{1.8}Mn\textsubscript{2}O\textsubscript{7}–xF\textsubscript{2}), with excellent cycle stability and rate capability. Surprisingly, despite the close-packed perovskite-based structure, two extra fluoride ions are (de)intercalated beyond x = 2, leading to a reversible capacity of 1168 mAh/cm\textsuperscript{3} (0 ≤ x ≤ 4). During the further intercalation, oxygen molecules are formed in the perovskite layer, as in Na\textsubscript{0.75}[Li\textsubscript{0.25}Mn\textsubscript{0.75}]O\textsubscript{2}, which is responsible for the charge compensation (i.e. anion redox)\textsuperscript{5,6} and the concomitant formation of oxygen vacancies that allow the incorporation of the excess fluoride ions. These results highlight the layered perovskite oxide/oxyfluorides as a new class of active materials for the construction of high-performance FIBs. More generally, the concept of anion-intercalation through O\textsubscript{2} formation in the mixed-anion perovskite materials can be used to develop new functionalities.
Introduction

Considerable efforts have been devoted to developing efficient energy storage systems in order to achieve a green and sustainable energy society in the future. The widespread success of lithium-ion rechargeable batteries (LIBs) is attributed to their high energy density, light weight, long-term durability, and the presence of a large number of available host structures. In recent years, special attention has been paid to enhancing the capacity of cathode materials through the redox of oxide anions (including the formation of \( \text{O}^- \), \( \text{O}_2^- \), \( \text{O}_2 \), and even \( \text{O}_3 \)), in addition to the redox of transition metal cations. However, there is a growing demand for electric vehicles with longer mileage and grid energy storage, for which developing larger power source is required.

In order to meet these requirements, various types of batteries (e.g., all-solid-state, air battery type, redox flow type) using different carrier ions (e.g., \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{Mg}^{2+} \), \( \text{Cl}^- \), \( \text{F}^- \)) have been proposed. Among them, fluoride ion batteries (FIBs) with fluoride ions working as a carrier are highly promising with respect to theoretical high energy densities. The highest electronegativity of fluorine as well as high redox potential 2.87 V (vs. SHE) of \( \text{F}^-/\text{F}^2^- \) (cf. 1.36 V for \( \text{Cl}^-/\text{Cl}^2^- \), 0.54 V for \( \text{I}^-/\text{I}^2^- \)) allow the wide electrochemical potential window, leading to high voltage batteries. A high
electrochemical capacity per weight in conversion-type fluorine-rich compounds (e.g., CuF₂, BiF₃, MgF₂) is also an advantage. However, a drastic decrease in electronic conductivity and a large volume change during charge-discharge process seriously impairs rate capability and cycle stability.

For these reasons, as an alternative to the conversion type, the search for electrode candidates from materials capable of topotactic fluorine intercalation appears to be promising, as has been with the case of LIBs (e.g., LiCoO₂ and LiCo₀.₃Ni₀.₃Mn₀.₄O₂). O. Clemens et al. showed electrochemical topotactic fluorinations, using LaSrMnO₄, La₂CoO₄ and more recently La₁.₃Sr₁.₇Mn₂O₇ with a Ruddlesden-Popper perovskite structure of Aₙ₊₁BₙO₃ₙ₊₁ (n = 1, 2), in which A is a rare-earth or alkaline earth element and B is a transition metal. Unfortunately, they all exhibited low reversible discharge capacities of 100 mAh/g (~1.3 F per LaSrMnO₄), 60 mAh/g (~0.9 F per La₂CoO₄), 25 mAh/g (~0.5 F per La₁.₃Sr₁.₇Mn₂O₇). The achieved rate capability is also low for all materials, with poor discharge capacities even at low current densities of 2.4~12 µA/cm² at 150~200 °C.

In this study, we demonstrate that La₁.₂Sr₁.₈Mn₂O₇F₂ is able to electrochemically deintercalate (and intercalate) two fluoride ions by fully utilizing the interstitial site in
the rock-salt slab, with excellent cycle performance (80% capacity retention after 50 cycles) and rate capability (60 mAh/g at 100 mA/g). Unexpectedly, La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ can be further topotactically fluorinated to a capacity density of 1168 mAh/cm$^3$, allowing the development of FIBs with high energy density and durability. Interestingly, these excess fluoride ions are introduced into the perovskite slabs, where the charge compensation and space creation is achieved through the formation of molecular $\text{O}_2$ (i.e., anion redox), as found in LIBs and sodium ion batteries$^{5,13,14,37,38}$. Given the abundance of perovskite compounds, these results are expected to facilitate the development of cathode materials for FIBs, as mixed-anion compounds with anion redox could be applied to active materials.
Results and Discussion

Structural characterization of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$

We employed a chemically fluorinated La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ as a starting cathode active material. According to the previous report$^3$, La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ was fluorinated using polyvinylidene difluoride. X-ray diffraction (XRD) data (Supplementary Figure 1) yielded tetragonal ($I4/mmm$) cell parameters ($a = 3.88065(7)$ Å, $c = 20.1203(4)$ Å for La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ and $a = 3.7956(3)$ Å, $c = 23.349(2)$ Å for La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$) that are consistent with those reported$^3$. The observation with Spherical Aberration (Cs) corrected Scanning Transmission Electron Microscope (Cs-corrected STEM) for these samples are also consistent with the reported structures, while atomic-resolution electron energy loss spectroscopy (EELS) for La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ revealed the fluorine insertion at the interstitial site in the rock-salt block (Supplementary Figures 2, 3). Observation by Scanning Electron Microscopy (SEM) show that the shape and size of the primary particles (1 ~ 3 µm) are retained after chemical fluorination (Supplementary Figure 4).
Figure 1 | Electrochemical performance of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ and structural changes after discharge/charge process. 

a, Discharge/charge curves at a rate of 10 mA/g at 140 °C, where red and blue lines show, respectively, cell voltage and potential of counter electrode. 

b, XRD patterns of cathode composites containing La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ before and after galvanostatic discharge/charge. Red and black broken lines are peaks of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ and La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$, respectively. Asterisk marks La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ (solid electrolyte). 

c, High-angle annular dark-field (HAADF) STEM images of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ after discharge and 1 cycle viewed along [010]. 

d, Discharge/charge scheme of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$. Note that the pristine sample has an oxygen off-stoichiometry of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$. (see text).
Electrochemical intercalation in rock-salt slabs of \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\text{F}_x (0 \leq x \leq 2) \)

A cathode mixture was prepared by ball-milling \( \text{La}_{x.3}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\text{F}_2 \) with \( \text{La}_{x.9}\text{Ba}_{0.1}\text{F}_2 \) and Vapor-Grown Carbon Fiber (VGCF), as often used in FIBs\(^{34,35} \). A three-electrodes cell was assembled using the mixture, with Pb wire as a reference electrode by inserting its tip into the solid electrolyte not to contact with each electrode layer. Figure 1a shows discharge-charge profiles in a voltage range of \(-1.5~2.0\) V at 10 mA/g. Upon the initial discharge, the capacity reached 91.2 mAh/g, which is equivalent to the capacity of two F anions (91.7 mAh/g) and suggests an almost complete F extraction from the \( \text{La}_{x.3}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\text{F}_2 \). Subsequent charge process yielded a capacity of 86.8 mAh/g, corresponding to a discharge-charge efficiency of 95.2%.

Structural changes in the cathode material during the discharge-charge reactions were probed by \textit{ex-situ} XRD in Ar atmosphere (Figure 1b). Upon discharge, the pristine \( \text{La}_{x.3}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\text{F}_2 \) (I4/mmm) is transformed to \( \text{La}_{x.3}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7 \) (I4/mmm; \( a = 3.842(2) \) Å, \( c = 20.25(2) \) Å), and then, after charging, converted to the original \( \text{La}_{x.3}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\text{F}_2 \) (\( a = 3.781(34) \) Å, \( c = 23.32(21) \) Å). No change of the diffraction peaks in \( \text{La}_{x.9}\text{Ba}_{0.1}\text{F}_2 \) is observed. HAADF–STEM images (Figure 1c, Supplementary Figure...
5a, 5b) and SAED patterns (Supplementary Figure 5c, 5d) of the La\textsubscript{1.2}Sr\textsubscript{1.8}Mn\textsubscript{2}O\textsubscript{7}F\textsubscript{2} cathode after discharge and 1-cycle agree with the proposed structures. These observations verify a reversible electrochemical (de)intercalation between La\textsubscript{1.2}Sr\textsubscript{1.8}Mn\textsubscript{2}O\textsubscript{7}F\textsubscript{2} and La\textsubscript{2}Sr\textsubscript{2}Mn\textsubscript{2}O\textsubscript{7} (Figure 1d). Atomic-resolution STEM–EELS mapping supported the insertion and extraction of fluoride ions, but the atomic contrast (Supplementary Figure 6) is less clear than the pristine La\textsubscript{1.2}Sr\textsubscript{1.8}Mn\textsubscript{2}O\textsubscript{7}F\textsubscript{2} sample, where all F\textsuperscript{−} ions in are occupied at the interstitial site of the rock-salt slabs.
Figure 2 | Cycle stability and rate performance of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$. a, Cycle performance of the discharge and charge capacities and the efficiencies. The efficiencies are estimated by dividing charge capacities by discharge capacities in the same cycle. b, Rate capability of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$, which was charged to 2.0 V at different rates and then discharged to -1.5 V at the same rate as the charge process. c, d, HAADF-STEM images of charged La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ after 50 cycles, viewed along [010]. Note that the pristine sample has an oxygen off-stoichiometry of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_2$ (see text).
It is remarkable that the electrode $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\text{F}_2$ exhibited excellent cycle stability and rate capability. It maintained capacity retention at 80% of the initial capacity after 50 cycles, with the coulombic discharge-charge efficiency of almost 100% during the cycles (Figure 2a). Moreover, even at 100 mA/g, this electrode has a capacity of 60 mAh/g (corresponding to 65% of the discharge capacity at 10 mA/g), despite the relatively large particle size of 1~3 μm (Figure 2b). These properties are distinct from conversion-type active materials (e.g., $\text{CuF}_2$, $\text{BiF}_3$) whose capacity drops rapidly; in the case of $\text{BiF}_3$, it is less than 50% of the initial discharge capacity after 10 cycles.

The HAADF-STEM images after 50 cycles at charge state (Figure 2c, 2d) resembles those of the pristine sample of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7\text{F}_2$, with no cracks in the active material or voids at the active/solid electrolyte interface in the electrode (Figure 2c, Supplementary Figure 5a, 5b). It may be related to a smaller volume change of our material (10%) than reported cathode materials of FIBs (e.g., $\text{CuF}_2$ (173%), $\text{BiF}_3$ (134%), $\text{LaSrMnO}_2\text{F}_x$ (17%), $\text{La}_2\text{CoO}_4\text{F}_x$ (13%)).

We also conducted electrochemical measurements using $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ as a starting material and obtained similar charge/discharge curves with excellent cycle stability.
(Supplementary Figure 7). Compared with La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$F$_x$, XRD and STEM–EELS data (Supplementary Figure 8) show a difference in the 1st charge process, while subsequent cycles are reversible (Supplementary Figure 7), with the charge/discharge profiles similar to those of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$. We also found that the Mn K-edge shifts to lower energy after the 1st cycle than that of pristine La$_{1.2}$Sr$_{1.8}$Mn$_{3.4+2}$O$_7$ (Supplementary Figure 9), indicating a reduced valence to Mn$^{3+}$. This implies that the initial F intercalation to La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ leads to a partially loss of oxide anions, resulting in La$_{1.2}$Sr$_{1.8}$Mn$_{0.5+2}$O$_7$. The insertion of two F (i.e., redox from Mn$^{3+}$ to Mn$^{4+}$) determines the oxygen vacancy to be around 0.4. Furthermore, the change of Mn K-edge in La$_{1.2}$Sr$_{1.8}$Mn$_{3.4+2}$O$_7$F$_x$ from the pristine to the discharged state is similar to that of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ from the charged to 1-cycled discharged state, suggesting that the pristine oxyfluoride already has oxygen vacancies. Thus, in the following it is referred to as La$_{1.2}$Sr$_{1.8}$Mn$_{0.5+2}$O$_7$F$_x$ ($\delta \sim 0.4$).

**Electrochemical further fluorination of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$–xF$_x$ ($0 \leq x \leq 4$)**
So far, we have demonstrated the excellent performance of electrochemical reactions for La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_{7-\delta}$F$_x$ ($0 \leq x \leq 2$). Although La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ is the terminal F-rich phase available via chemical fluorination\cite{28,30}, recent studies on oxides for LIBs successfully utilize oxygen redox chemistry (O$^2$/O$^-$) to achieve extended capacity (e.g., Li$_{1.0}$Mn$_{0.5}$Co$_{0.13}$Ni$_{0.13}$O$_2$, Li$_{0.15}$Ru$_{0.75}$Sn$_{0.25}$O$_3$, Li$_{1.3}$Nb$_{0.3}$Mn$_{0.4}$O$_2$). With this in mind, we attempted further fluorination by increasing the upper cut-off potential (from 2.0 V) and the results are shown in Figures 3 and Supplementary Figure 10. Here, a cell with PbF/AB (acetylene black) composite (in addition to Pb foil) was employed on the anode side to allow excess fluoride ions to path through the La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ cathode. When the electrochemical cell was charged to 3.0 V after the initial discharge (with a capacity equivalent to two fluoride ions), a wide plateau appeared at around 2.0 V and the total charge capacity reached about 250 mAh/g (Figure 3a). The subsequent discharge process delivered a large capacity of 190 mAh/g, twice the capacity of the initial discharge process. Similar results were obtained with La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ as the starting material (Supplementary Figure 11).
Figure 3 | Charge/discharge properties and structural changes of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$–$\delta$F$_2$ upon charging at higher potential. a, Charge/discharge curves at a rate of 10 mA/g at 140 °C, where PbF/AB composite was included in the anode side between solid electrolyte and Pb foil as a fluorine source. b, XRD patterns of cathode composites containing La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$–$\delta$F$_2$ before and after galvanostatic charge/discharge. Red and black broken lines correspond, respectively, to La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$–$\delta$F$_2$ and La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$. Asterisks denote La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ electrolyte. Note that in order to obtain clearer diffraction peaks for La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$–$\delta$F$_2$, we used a cathode composite with higher active material.
content (~60 wt%) (see Supplementary Figure 12). \( c \), Atomic resolution STEM-EELS mapping images of \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7–\delta\text{F}_2 \) before and after galvanostatic charge/discharge, viewed along [010]. For simplicity, the ideal structures are shown.

This excess electrochemical fluorination is also topotactic; the XRD pattern of the 3.0 V charged \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7–\delta\text{F}_2 \) cathode is similar to that of the pristine cathode (Figure 3b), and the ADF images of these cathodes show regular cation arrangements (Figure 3c). Furthermore, the atomic-resolution EELS mapping in the 3.0 V charged cathode (Figure 3c) shows an excess of fluoride ions in the perovskite block, in addition to the interstitial site in the rock-salt slabs. The intensity of XRD pattern of the 3.0 V charged cathode is close to that of the pristine \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7–\delta\text{F}_2 \). The following discharge process led to the de-fluorinated \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7–\delta\text{F}_2 \), as confirmed by XRD and EELS (Figure 3b, 3c).
Figure 4 | Electrochemical properties of La$_{x}$Sr$_{y}$Mn$_{2}$O$_{7-δ}$F$_{2}$ upon further fluorination. a, Cycle performance of discharge/charge capacities and the efficiency. The efficiency was calculated as follows: the $n$-th discharge capacity divided by the $n$-th charge capacity. b, Discharge curves with different current rates for La$_{x}$Sr$_{y}$Mn$_{2}$O$_{7-δ}$F$_{2}$ after 15 cycles. The same conditions were adopted for charging, with an upper limit potential of 3.0 V and a current rate of 10 mA/g. c, Plots of the volumetric/gravimetric capacities for La$_{x}$Sr$_{y}$Mn$_{2}$O$_{7-δ}$F$_{2}$ and cathode materials reported in LIBs$^{[12,39,40]}$. 
The capacity of each cycle provides about 200 mAh/g (four electrons reaction), and the capacity reversibility of the charge/discharge remains close to 100% as shown in Figure 4a, except for the first discharge/charge process at 80% efficiency. The origin of the irreversible charge capacity on the 1st cycle is not clear, but may include side reactions such as the decomposition of the solid electrolyte La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ (Supplementary Figure 10) and partial oxygen release as reported in LIBs$^{41-43}$. Discharge capacities increase gradually with the charge-discharge cycle and remain stable for at least 30 cycles without obvious decrease in capacity, and the reversible capacity amounts to 1168 mAh/cm$^3$. As shown in Figure 4c, this value is much higher than that of typical LIB cathode materials and, in terms of volumetric energy density, is comparable to that of recently investigated active materials using anion redox$^{8,12}$. Figure 4b shows that our material with a fluorine content varying between $x = 0$ and 4 has a relatively high rate capability (200 mAh/g at 100 mA/g), which is possibly related to the rapid fluoride ion diffusion in the bulk.
Anionic redox reactions

The charge compensation mechanisms of (de)fluorination were examined by synchrotron hard/soft X-ray absorption spectroscopy (XAS) (Figure 5 and Supplementary Figure 13). While the La $L$ and Sr $K$ absorption edges are unchanged, the Mn $L$-edge peak shifts to higher energies in the early stage of fluoride ion insertion ($x < 2$) and then remains unchanged in the later stage ($2 < x < 4$). These results suggest that the oxidation of Mn$^{3+}$ ions occurs only in the early stage of fluoride ion insertion.

In the O $K$-edge spectrum, a broad peak, which is attributed to the transitions from the O 1$s$ level to the hybridized states of the Mn 3$d$ and O 2$p$ orbitals, was observed around 530 eV before charging ($x \sim 0$). The intensity at 529 eV increased in the early stage of fluoride ion insertion ($x < 2$) (Figure 5b), which is explained by the crystalline field stabilization energy via oxidation of Mn$^{3+}$ ($d^4$, high spin) to Mn$^{4+}$ ($d^3$). The same behavior is seen in the Mn $L$-edge spectra (Figure 5a). On the other hand, further fluorination beyond $x \sim 2$ resulted in the emergence of a new O $K$-edge peak at around 530.8 eV, and this peak increases its intensity with $x$, while it reversibly disappears upon fluorine deintercalation. A similar peak has been observed in peroxides such as Li$_2$O$_2$ and also in lithium-rich cathodes containing oxidized oxygen species (e.g., O$^-$,
These observations strongly suggest that in our oxyfluoride cathode, oxidized oxygen species are involved in charge compensation during the charge/discharge process for \(2 < x < 4\).

To further elucidate the nature of oxidized oxygen species, resonant inelastic X-ray scattering (RIXS) measurements from 528.5 to 533.0 eV in O K-edge XAS spectra were performed (Supplementary Figure 14). The obtained RIXS spectra at 530.8 eV (Figure 5c) exhibited discrete energy-loss peaks around the elastic line from 5 to 0 eV, representing several vibrational levels of the ground state potential energy surface. The frequency of the first vibrational level was approximately 1600 cm\(^{-1}\), similar to the gaseous molecular O\(_2\) bound with Mn\(^{1+}\), and differed from 1108 cm\(^{-1}\) in O\(_2\) and 743 cm\(^{-1}\) in O\(_2^+\). Since the RIXS measurements were performed under high vacuum, this oscillatory signal is attributed most likely to O\(_2\) molecules in La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_{7-\delta}\)F\(_x\), rather than those in the gas phase or absorbed on the cathode surface. Such O\(_2\) formation has recently been observed in Na\(_{0.75}\)[Li\(_{0.25}\)Mn\(_{0.75}\)]O\(_2\) during charge process (i.e., Na-deintercalation). The greater polarization of the anion redox region (\(x > 2\)) of La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_{7-\delta}\)F (Figure 3a) and Na\(_{0.75}\)[Li\(_{0.25}\)Mn\(_{0.75}\)]O\(_2\) compared to Li\(_2\)Ru\(_{0.75}\)Sn\(_{0.25}\)O\(_3\) (in which redox via O\(_2^+\) occurs) is also in line with the formation/annihilation of O\(_2^+\).
In the pre-edge region of F K-edge spectra (Figure 5d and Supplementary Figure 15), a small peak attributed to metal-fluorine bond appears with the insertion of fluoride ions, and its intensity increases significantly when \( x > 2 \), indicating that the formation of \( O_2 \) is accompanied by the formation of the Mn-F bond in the perovskite blocks of \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7-x\text{F}_x \). This result explains why \( \text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7-x\text{F}_x \) can host an excess of F beyond the oxide deficiency (\( \delta \sim 0.4 \)): the formation of \( O_2 \) is not only responsible for oxidation, but also creates additional anion vacancies and allow excess fluoride ions to fill these sites. Note that similar molecular-like \( O_2 \) state are formed in electrode materials of sodium ion battery during charge (i.e., Na-deintercalation) process. The formation of four-electron oxidized \( O_2 \) rather than \( O_3 \) or \( O_3^2- \) may be related to the shorter intramolecular distance of \( O_2 \), which makes it easier to fit into the perovskite space. It is currently unclear, for example, at which oxygen sites in the perovskite slab the molecular-like \( O_2 \) states are produced, for which, e.g., an operando STEM observation is required.
Figure 5 | Changes in electronic structures for La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_{7-\delta}$F$_x$ on 1st charge/discharge process. **a, b**, Changes in XAS spectra collected for various states in charge/discharge profiles shown in Figure 3a. **a**, Mn $L$-edge absorption and **b**, O $K$-edge absorption. The $x$ in the figure represents the fluoride content ($x$ in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_{7-\delta}$F$_x$). **c**, Oxygen $K$-edge XAS and high-resolution RIXS spectra recorded at excitation energies of 530.2 and 530.8 eV for in (lower) pristine and (upper) charged (3.0 V) states, respectively. The vibrational frequency of around 1600 cm$^{-1}$ indicates the presence of O. **d**, F $K$-edge absorption, indicating the formation of Mn-F bond at $x > 2$. 
Outlook for intercalation-type active material

We demonstrated electrochemical intercalation of fluoride ions with excellent reversibility, cyclability and rate capability, using the double-layered Ruddlesden-Popper type perovskite oxyfluoride La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_{7-\delta}$F$_x$. Interestingly, in addition to the conventional Mn redox at $0 < x < 2$, this oxyfluoride can incorporate excess fluoride ions ($2 < x < 4$) into the perovskite blocks by forming molecular O$_2$ species (anion redox). It should be emphasized that, like the LIB, the current FIB has room for further improvement in terms of electrochemical properties such as cycle stability, rate characteristics, and fluoride ion diffusion; available strategies include chemical substitution with other transition metals, optimization of composition in an electrode mixture and tuning particle morphologies, in addition to modification of solid-solid interfaces with solid electrolytes (e.g., surface coating, orientation control).

Given the variety of structures and compositions known for conventional perovskite materials, the ability to capture excess fluorine ion through the formation of O$_2$ molecules adds a new dimension to perovskite engineering not only for battery research but also for other disciplines. In fact, formation of molecules at the anion site in perovskite ABO, with the ‘closed packed’ structure is not obvious, as seen in the
theoretically predicted H₂ molecule in SrTiO₅, and could be an interesting research topic in general. Furthermore, this study sufficiently raises awareness that electrochemistry is a powerful tool for obtaining novel oxyfluorides and, more generally, mixed-anion compounds that could have an impact on a variety of physical and chemical functions.

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Methods

Synthesis of materials. La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ was prepared by using conventional solid state reaction similar to previously described$^4$. Reagent grade of La$_2$O$_3$ (99.99%, Kojundo Chemical Laboratory), SrCO$_3$ (99.9%, WAKO pure chemical industries, ltd.) and MnO (99.5%, WAKO pure chemical industries, ltd.) were used as starting materials. These materials were weighed in a stoichiometric ratio and mixed by planetary ball-milling for 10 h. This mixed powder was pressed into a pellet and annealed at 1400 °C for twice of 20 h in air with an intermediate grinding. La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$-$\delta$F$_2$ was synthesized from chemical fluorination of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ using polyvinylidene difluoride (PVdF) as previously reported$^3$. 1.0 g of the obtained La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ powder and 1.5 g of PVdF (Aldrich, average Mw: ~180,000, average Mn: ~71,000) were placed in separate alumina boats, covered with a sagger in an electric muffle furnace, and heated at 400 °C for 10 h under air. La$_{0.9}$Ba$_{0.1}$F$_{2.9}$, using as a solid electrolyte with fluoride-ion conductivity, was synthesized as reported in the literature$^5$. LaF$_3$ (99.9%, Kojundo Chemical Laboratory) and BaF$_2$ (99.9%, Kojundo Chemical Laboratory) were mixed in a molar ratio of 9:1 and ball-milled at 600 rpm for 12 h using Ar-filled 45 mL ZrO$_2$ pot and 30 g of $\Phi$5 mm balls. The mixture was annealed at 600 °C for 10 h in Ar atmosphere.
Assembly of the all-solid-state type electrochemical cell. The cathode composite consisted of La_{1.2}Sr_{1.8}MnO_{2-δ}F_{2} (or La_{1.2}Sr_{1.8}MnO_{7}) powder, La_{0.9}Ba_{0.1}F_{2.9} powder and Vapor-Grown Carbon Fiber (Showa Denko, VGCF, battery grade), with mixed in a weight ratio of 30:60:10 by ball-milling for 10 h at 100 rpm using 45 mL of ZrO_{2} pot and 30 g of ZrO_{2} balls. La_{0.9}Ba_{0.1}F_{2.9} and 0.2 mm thickness of Pb foil were used as a solid electrolyte and an anode, respectively. Additionally, in case of examination of further fluorination and La_{1.2}Sr_{1.8}MnO_{7} cathode, PbF_{2}/acetylene black (Denki Kagaku Kogyo, AB) composites, mixed by ball-milling for 3 h at 600 rpm, are used as a fluorine source on anode side. The electrochemical cells were assembled in disk-shaped pellet by compressed cathode/solid electrolyte/anode layers. At first, 10 mg of cathode composite and 200 mg of La_{0.9}Ba_{0.1}F_{2.9} were compressed heating at 120 °C for 45 min under 4 ton/cm^{2}. After that, Pb foil (and PbF_{2}/AB composite) was added as an anode layer and Pt foils were added on both ends as a current collector. These layers were compressed under 4 ton/cm^{2}. The diameter of the pellet was 11.28 mm. All fabrication processes of the all-solid-state type electrochemical cell were conducted under Ar atmosphere in a glovebox.

Electrochemical measurement. Assembled cells were put in a sealed container without exposing to the air atmosphere. Charge and discharge experiments of the all-
solid-state fluoride ion cells were conducted in a potential range –1.5~2.0 (or –1.5~3.0) V vs. Pb/PbF₂ at 140 °C heated by mantle heater. The lower cut-off potential was set at –1.5 V since La₁₀.₉Ba₁₀.₁F₂₉ (in the cathode) decompose under –2.4 V vs. PbF₂/Pb. Unless otherwise specified, 6.7 mA/g was applied as the current density. Rate dependence of the charge-discharge profiles were measured with various current densities at both charge and discharge process. Cyclic voltammetry was carried out with at a sweep rate of 1 mV/sec. The electrochemical properties of the electrochemical test cells were collected using a potentiostat/galvanostat apparatus (VMP3, Bio-Logic Science Instruments).

**Materials characterization.** XRD profiles of the material were obtained using Rigaku Ultima IV using Cu Kα radiation with 40 kV of tube voltage and 40 mA of current. Spherical Aberration (Cs) corrected scanning transmission electron-microscope (Cs-corrected STEM) observations and selected area electron diffraction (SAED) measurements were collected using JEM-ARM200F (JEOL) to characterize the crystal structures of the samples. Thin sections of the samples were fabricated by cryo-focused ion beam (cryo-FIB) micro-sampling technique using nanoDUE’T NB5000 (HITACHI). Atomic resolution electron energy loss spectroscopy (EELS) mapping and energy dispersive X-ray spectroscopy (EDX) were obtained to investigate the
elements ordering and the position of fluorine element in the crystal structures of samples. Synchrotron XRD was measured at BL02B2 beamline in SPring-8 in Japan. X-ray absorption spectroscopy (XAS) was measured at BL14B2 and BL27SU beamlines in SPring-8 in Japan. Resonant inelastic X-ray scattering (RIXS) measurements were performed at BL07LSU in SPring-8 using a high resolution spectrometer. The sample powders were supported on the carbon tape in the glove box filled with inert Ar gas and transferred to the measurement chamber without exposing atmosphere. The sample positions were changed at 2.4 μm/s during the RIXS measurement to avoid radiation damage.
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Author contributions

H. M. designed and conducted the experimental work. H. M., H. N., K. Y. and T. Y. prepared materials and measured electrochemical properties. H. M. carried out the analysis of the crystal structure by XRD measurement and STEM observation. K. Y., H. N., T. Y. and K. N., with comments from Y. U., measured and analyzed XAS spectra.
J. M. and Y. H. measured and analyzed RIXS spectra. H. M., K. Y., Y. U. and H. K. wrote the manuscript. All authors discussed the results.