Electrochemical Oxidative Fluorination of an Oxide Perovskite

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Experimental Methods

Materials Synthesis. Nanoparticles of ReO_3 were prepared using a method previously employed by our group.^{1,2} In a typical preparation, a 0.1 M solution was prepared by dissolving Re_2O_7 in methanol, and then evaporating on a glass plate that was heated at 250°C for 5 minutes in a convection oven, until the methanol had completely evaporated. The reduction of Re_2O_7 produced ReO_3 , which was deposited as a brick red film on the glass plate. The film was removed from the plate and ground *via* mortar and pestle to yield a deep red metallic powder. The as-prepared samples were dried under vacuum at 110 °C before electrochemical cell preparation.

Materials Characterization. Laboratory X-ray powder diffraction (XRPD) patterns were collected on a Bruker D8 Advance diffractometer with a Cu K_{α} source, equipped with a LynxEye XE-T detector. Neutron total scattering measurements of *ex situ* samples was performed at the NOMAD beamline at the Spallation Neutron Source at Oak Ridge National Laboratory.³ Data were normalized against a vanadium rod, the background was subtracted and the total structure factor were transformed into pair distribution function (PDF) data using specific IDL codes developed for the NOMAD scattering instrument with a Q range of 0-25 Å and a pseudo-voigt polynomial H correction.

Operando synchrotron X-ray powder diffraction (SXRD) patterns were collected at the Advanced Photon Source, Argonne National Laboratory using the AMPIX electrochemical cell, following the method detailed by Borkiewicz et al.⁴ SXRD collection was performed in transmission geometry through the cell windows, using a monochromated X-ray beam with ($\lambda = 0.25463$ Å) and a PerkinElmer 2D Plate Detector. GSAS-II software was used to integrate patterns into the intensity vs. 2 θ format displayed.⁵

sXAS and XES measurements were performed at the iRIXS endstation at beamline 8.0.1 at the Advanced Light Source. Absorption spectra were collected in total electron yield (TEY) and total fluorescence yield (TFY) modes. A TiO₂ reference was used for excitation energy calibration of the O K-edges The emission energies was calibrated using F 1s and O 1s core level energies for F K- and O K-edges respectively. F 1s and O 1s core levels were obtained by X-ray Photoelectron Spectroscopy (XPS) measurements performed using a Phi VersaProbe 5000 system at the Analytical and Diagnostics Laboratory (ADL), Binghamton University.

Transmission Electron Microscopy (TEM) images were collected on a JEOL JEM2100F with an operating voltage of 200 kV. Samples for TEM analysis were prepared by drop-casting a suspension of the powder in ethanol onto a 200 mesh Cu grid coated with a lacey carbon film followed by drying under vacuum. *Ex situ* samples for all measurements were prepared by collecting pure $F_x \text{ReO}_3$ electrodes from disassembled electrochemical cells cycled to the desired state of charge and washing the material in dimethyl carbonate in an argon glovebox.

Electrochemical Characterization. Several methods were developed for preparing fluoride ion batteries with both liquid and solid electrolytes to enable different aspects of testing. All cell components and electrodes were dried under vacuum at 110 $^{\circ}$ C for 1 hour before assembly and cell assembly was performed in an argon glovebox.

Stainless steel Swagelok cells were employed for electrochemical testing and were equipped with borosilicate glass fiber pads (Whatman GF/D) soaked with electrolyte solution. 1 M Tetrabutylammonium Fluoride in tetrahydrofuran (TBAF) was used as the liquid electrolyte. Thick film electrodes were prepared by blending 10 wt% graphite powder (300 mesh), 10 wt% acetylene black, 20 wt% polytetrafluroethylene (average particle size of 1 μ m), and 60 wt% active material, and pressed under a hydrostatic pressure of 0.9 tons. The electrodes had a typical mass loading of 4.5 mg cm². Film electrodes of pure ReO₃ as the active material were also prepared by depositing onto Ni foil disks with a typical mass loading of 4.5 mg cm².

Solid state cells were prepared with a film of Ba-doped LaF₃. Tysonite-type barium-doped lanthanum fluoride (LBF) electrolyte of composition $La_{0.95}Ba_{0.05}F_{2.95}$ was prepared by a co-precipitation method described elsewhere, and used as the solid electrolyte.⁶ In a typical synthesis, stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$ and $Ba(NO_3)_2$ were dissolved in de-ionized (DI) water followed by the dropwise addition of an aqueous solution of NH_4F . The precipitate was collected by centrifugation, washed with DI water and dried at 80 °C overnight. The resulting powder was then mixed with 5 wt% polyvinylidene fluoride (PVDF) binder in n-methyl-2-pyrrolidone (NMP) solvent, cast on an aluminum foil, and dried at 110 °C under vacuum. The layer was then peeled off to create a free-standing 100 micrometer thick film of LBF electrolyte. Similarly, an active electrode was prepared by mixing 30 wt% ReO₃ active material, 50 wt% LBF electrolyte, 10 wt% PVDF and 10 wt% SuperP carbon with a minimal amount of NMP to form a slurry which was cast on aluminum foil and dried at 110 °C under vacuum. A copper fluoride electrode was cast onto copper foil using the above method and contained 70 wt% anhydrous CuF₂, 20 wt% SuperP carbon and 10 wt% PVDF.

All-solid-state fluoride ion battery cells were assembled by pressing ReO₃ electrodes, LBF electrolyte layer and CuF₂ counter electrodes together into 10 mm diameter pellets using a hydraulic press at a pressure of 1300 kg cm⁻² for 30 minutes. The pellet was inserted into a Swagelok cell inside an argon-filled glovebox, and electrochemical testing was performed at 150 °C.

Electrochemical impedance spectroscopy (EIS) measurements were carried out using a VersaStat MC electrochemical workstation over the frequency range of 1 MHz to 0.1 Hz with a sinusoidal excitation voltage of 10 mV. The measurements were done under open circuit condition at various levels of fluoride intercalation.

Operando synchrotron XRD patterns were collected using an AMPIX electrochemical cell equipped with two glassy carbon windows.⁴ The same glass fiber separators, metallic counter electrodes, and electrolyte solutions described previously were used during all *operando* experiments.

Differential Electrochemical Mass Spectrometry. The custom-built differential electrochemical mass spectrometry (DEMS) system and the cell geometry used is described in detail in previous publications.^{7,8} In brief, electrochemical half cells of modified Swagelok design were assembled in an argon filled glovebox using a ReO₃ working electrode (80 wt % ReO₃, 10 wt % Super P, 10 wt % PTFE) pressed onto a stainless steel mesh current collector, a TBAF soaked glass fiber separator, and a Cu metal counter and reference electrode. The electrochemical cells were

then attached to the DEMS system such that a head of positive argon pressure (1.2 bar) was maintained. During the measurements, argon gas pulses periodically swept the accumulated gases to a mass spectrometer chamber for identification of H_2 , O_2 , and F_2 .

Solid-State ¹⁹F NMR Spectroscopy Solid-state ¹⁹F MAS-NMR spectra were acquired on a Bruker AVANCE-III Ultrashield Plus 800 NMR spectrometer using a narrow-bore 18.8 T superconducting magnet and operating at a Larmor frequency of 752.980 MHz for ¹⁹F. Experiments were conducted using a 1.3 mm double-resonance H/F–X magic-angle spinning (MAS) probehead. For the solid-state NMR measurements, the conductive F_x ReO₃ powders were mixed with KBr powder in a roughly 1:5 ratio by mass to reduce effects of eddy currents on the spinning samples. KBr also served as an internal temperature probe for accurate determination of the sample temperature under the different measurement conditions. ^{9,10} One-dimensional (1D) ¹⁹F Hahn-echo MAS spectra were acquired at 23 kHz MAS unless otherwise specified, at 298 K, and using a 90°- τ -180°- τ pulse sequence with rotor-synchronized τ delay times of one rotor period and 90° radio frequency (rf) pulses of 3.5 μ s with a pulse power of 40 W. The ¹⁹F spin-lattice (T_1) relaxation times were measured by using a saturation–recovery pulse sequence with a Hahn-echo detection (Figure S12, Supporting Information). Isotropic ¹⁹F NMR chemical shifts were referenced to CFCl₃ using PTFE (-122 ppm) as a secondary standard.

Computational Thermodynamic Stability and Prediction of ¹⁹F NMR Chemical Shifts The CASM software package ^{11–13} was used to explore the phase stability of topotactic F insertion into perovskite ReO₃ by enumerating different F-vacancy orderings over the empty A sites of ReO₃. The energies of these configurations were calculated with DFT-PBE using the VASP plane-wave code and ^{14–17} the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) was used for the correlation and exchange potentials with a $17 \times 17 \times 17$ K-point mesh was used for all structures (*i.e.* ReO₃ and ReO₃F). Additionally, several configurations that allowed for a redistribution of Re or mixing between O and intercalated fluoride ions were considered.

¹⁹F NMR shielding tensors for various structural models were calculated using the fully periodic Gauge Including Projector Augmented Wave method (GIPAW)^{18–20} following a similar approach to Griffin and coworkers.²¹ In brief, a linear relationship between the calculated chemical shifts for several reference compounds were correlated to their experimentally observed values and fitted to establish relationship: $\delta_{iso}^{exp} = -k(\delta_{iso}^{calc} - \delta_{ref})$ where k = 0.68 and δ_{ref} = 160 from the fits as shown in S.I. Table T2 and S.I. Figure S10. This expression was then used to predict the experimentally observed chemical shift of the models considered in this work.

Computational Simulations of X-ray Spectroscopy Density functional theory (DFT) calculations to simulate the X-ray emission spectra were performed using the WIEN2k^{22,23} software package, which uses a full potential and linearized-augmented planewaves with local orbitals (LAPW + lo) to self-consistently solve the Kohn-Sham equations. Structures from the geometric relaxations in VASP were simulated without further optimization.²⁴ The O K-edge of

various intercalated forms were calculated using a planewave cutoff parameter, RKMAX, was chosen to be 6.5 and the cutoff between core and valence state set as -8.0 Ry. The effect of the core hole in simulation was characterize by performing partial core hole calculations, in which the unit cell is used instead of super cell to include the interaction between neighboring core holes. In the partial core hole approach, the occupancy of the core levels was reduced, and the missing charge was added as a uniform background charge to the unit cell to avoid re-normalization problems.^{25,26} For ReO₃F, the O K-edge calculations were performed six times due to the existence of six oxygen atoms at different sites, after which the average of the six individual contributions according to the multiplicity of each oxygen atom was calculated to obtain the theoretical O K-edge spectrum.

Operando X-ray Diffraction

Operando synchrotron X-ray diffraction was used in order to track average structural changes during the charging of $F_x \text{ReO}_3$, revealing a very small shift to higher angles of all peaks associated with ReO_3 . Throughout the charging process, no new peak formation is observed, as shown in Figure S1 and S2 due to the localized structural changes. However, a series of additional low angle peaks are seen (Figure S4), which are attributed to an SEI like layer which is formed from the decomposition of TBAF electrolyte. These peaks appear upon the addition of TBAF electrolyte, as shown in Figure S3 prior to electrochemical testing.



Figure S1: A heatmap of the *operando* synchrotron X-ray diffraction collected during the oxidative fluorination of ReO_3 displays diffracted intensity as a function of color. No new peaks are seen to form throughout the electrochemical charging process and reflections associated with cubic ReO_3 are maintained. We note a reduction in peak intensity beginning at higher states of charge.



Figure S2: *Operando* synchrotron X-ray diffraction shows no new peak formation throughout the charging process of $F_x \text{ReO}_3$, however we note the formation of a series of low angle peaks due to electrolyte decomposition. The spacing between each pattern is approximately 0.025 equivalent units of fluoride.



Figure S3: Upon the application of TBAF to ReO_3 electrodes, a series of additional XRD peaks are seen to form, associated with the decomposition of TBAF electrolyte. The XRD pattern shown in blue was collected on a ReO_3 electrode which was placed in a fully assembled AMPIX cell without any electrolyte. Once the electrolyte was added, a pattern (pink) was again collected prior to electrochemical measurement which showed the formation of a series of low-angle diffraction peaks.



Figure S4: A series of low angle peaks form due to electrolyte decomposition in the *operando* X-ray diffraction experiments. None of the peaks observed at low angles are associated with cubic ReO_3 . These peaks persist throughout the electrochemical charging process but do not vary in intensity or location. The spacing between each pattern is approximately 0.025 equivalent units of fluoride.



Figure S5: Throughout the initial oxidative fluorination process, diffraction peaks associated with ReO_3 steadily shift to higher angles, indicating a contraction of the unit cell. At high states of charge this abruptly reverses and the peaks of ReO_3 are seen to shift to lower angles, suggesting a decomposition of the material back to the original phase.



Figure S6: Comparison of simulated X-ray diffraction patterns of ReO_3 and FReO_3 in which F sits in the central A-site vacancy (see inset). The insertion of fluoride on the A-site does not produce any additional diffraction peaks, merely a slight contraction of the unit cell.

Impedance Spectroscopy

The slope of the real part of impedance vs ω , plotted in S.I. Figure S7(b), gives the Warburg factor (σ) that is inversely related to the diffusion coefficient (D), by the following equation where R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, F is the Faraday constant, and C is the molar concentration of F⁻ ions in the active material.

$$D = \frac{R^2 T^2}{2A^2 n^2 F^4 C^2 \sigma^2}$$
(1)

The calculated value of D at x = 0.2 is 1.75×10^{-16} cm² s⁻¹ which is in close agreement with the reported values of 3×10^{-15} cm² s⁻¹ for fluoride ion diffusion in oxyfluoride materials.²⁷ The D values drop to 2.5×10^{-18} cm² s⁻¹ and 5.7×10^{-19} cm² s⁻¹ at x = 0.4 and x = 0.5 respectively, as shown in S.I. Table T1, indicative of change in the mechanism for the oxidative process around this point, and is consistent between the liquid and solid-state cells.

Table T1: Calculated fluoride diffusion coefficients for various states of charge of $F_x ReO_3$.

x in $F_x ReO_3$	Diffusion Coefficient (D) cm ² s ⁻¹
$0.2 \\ 0.4 \\ 0.5$	$\begin{array}{c} 1.75 \times 10^{-16} \\ 2.5 \times 10^{-18} \\ 5.7 \times 10^{-19} \end{array}$



Figure S7: (a): Electrochemical impedance spectroscopy on all solid state cells demonstrate variations in the charge transfer resistance at different states of charge. As seen in the inset, the resistance rises slightly during fluorination. (b): Diffusion coefficients at different state of charge were calculated from the slope of a plot of $\omega^{-0.5}$ vs Z'.

Differential Electrochemical Mass Spectrometry



Figure S8: Differential electrochemical mass spectrometry identified H_2 evolution in fluoride ion battery half cells as well as CO_2 formation during the initial charge curve, due to electrolyte decomposition.



Figure S9: Quantitative differential electrochemical mass spectrometry showing the molar concentration of H_2 evolved during cycling. The four electron process at the higher voltage plateau of reflective of parasitic attack of the electrolyte at high voltages.

Solid State ¹⁹F NMR

Calculated NMR Shifts ¹⁹F NMR shielding tensors for various structural models were calculated using the fully periodic Gauge Including Projector Augmented Wave method (GIPAW)²⁰ following a similar approach to Griffin and coworkers.²¹ In brief, a linear relationship between the calculated chemical shifts for several reference compounds were correlated to their experimentally observed values and fitted to establish relationship: $\delta_{iso}^{exp} = -k(\delta_{iso}^{calc} - \delta_{ref})$ where k = 0.68 and $\delta_{ref} = -160$ from the fits. This expression was then used to predict the scale the calculated chemical shift of the models considered in this work to compare more directly with the experiments.



Figure S10: A plot of isotropic shieldings, δ_{iso}^{calc} vs δ_{iso}^{exp} for several fluorine-containing compounds was fit and the expression was used to scale calculated ¹⁹F chemical shifts for comparison with experimental data.

Table T2: Calculated ¹⁹F isotropic shieldings, δ_{iso}^{calc} , scaled calculated isotropic chemical shifts, $\delta_{iso}^{calc,scaled}$, and experimental ¹⁹F chemical shifts, δ_{iso}^{exp} , for several fluorine-containing compounds. Experimental values taken from Griffen *et al.* and the references therein.²¹

Compounds	site	δ_{iso}^{exp} (ppm)	σ_{iso}^{calc} (ppm)	$\delta_{iso}^{calc,scaled}$ (ppm)
AlF ₃	a	-172.8	-26.1	-177.3
CaF_2	a	-107	92.6	-96.6
CdF_2	a	-192.1	-38.2	-185.6
HgF_{2}	a	-196.4	-44.0	-189.4
$\mathrm{Hg}_{2}\mathrm{F}_{2}$	a	-95.8	105.4	-87.9
$KF-2H_2O$	a	-133	30.4	-138.9
LaF_3	a	-23.5	216.8	-12.1
	b	24.9	252.2	11.9
	\mathbf{c}	17.1	252.2	11.9
$Na_5Al_3F_{14}$	a	-190	-48.0	-192.2
	b	-166	-15.7	-170.2
	\mathbf{c}	-182	-44.8	-190.0
SrF_2	a	-84.1	118.0	-79.3
\mathbf{KF}	a	-130	36.0	-135.0
LiF	a	-204	-4.8	-162.8
NaF	a	-221	-83.4	-216.2
PbF_2	a	-20.5	190.9	-29.7
	b	-57.7	190.9	-29.7

Experimental ¹⁹F NMR Measurements Additional ¹⁹F NMR measurements were performed.



Figure S11: Solid-state 1D ¹⁹F echo MAS NMR spectrum acquired at 18.8 T, 298 K, 23 kHz MAS, with a recycle delay of 2 s for $F_{0.2}$ ReO₃ diluted 1:5 by mass with KBr. Partially resolved signals are observed at isotropic ¹⁹F chemical shifts of -136, -141, -150, -170, -174, and -189 ppm (dotted grey lines).



Figure S12: Solid-state ¹⁹F Hahn-echo MAS NMR saturation-recovery data for $F_{0.2}$ ReO₃. Normalized integrated ¹⁹F signal intensity is plotted as functions of the τ delay time for signals with isotropic chemical shifts of (a) -136 ppm, corresponding to a spin-lattice relaxation time T_1 of 4.0 s, and (b) -150 ppm, corresponding to a T_1 value of 0.3 s; the latter is representative of the other signals at -141, -170, -174, and -189. The solid-state ¹⁹F Hahn-echo NMR spectra were acquired for $F_{0.2}$ ReO₃ diluted 1:5 by mass with KBr, and acquired at 18.8 T, 23 kHz, and 298 K.

Table T3: Spin-lattice relaxation times associated with the different resolved ¹⁹F signals of $F_{0.2}ReO_3$, measured at 18.8 T, 23 kHz MAS, and 298 K from solid-state ¹⁹F Hahn-echo saturation recovery MAS NMR spectra

Chemical Shift (ppm)	Relaxation Time (sec)
-136	4.0
-141	0.3
-170 -174	0.4 0.4
-189	0.3

X-ray Emission and X-ray Absorption Spectroscopy

In order to characterize changes to the oxygen and fluoride environments, XES and XAS measurements were conducted on the F and O K-edges. This allowed for identification of changes in the band structure and the local environment. DFT calculations were then performed on a number of candidate crystal structures in order to simulate XES and XAS spectra for comparison to the experimental results. As shown in main text Figure 6, the experimental data was found to be well fit by a model in which Re migrated from an octahedral to a tetrahedral environment to bond to the inserted fluoride ion in the so-called $F_x \text{ReO}_3$ - 1F structure. A series of other structures were also considered and the predicted O K-edge XES and XAS structures are shown below. The experimental results are shown on the bottom while the calculated results are shown on the top panel for each given structural model.



Figure S13: Experimental data (red) compared to simulated X-ray emission and absorption patterns for 7-coordinate $FReO_3$ formed when Re migrates towards the face of an ReO_6 octahedra to form seven coordinate ReO_6F unit.



Figure S14: Experimental data (red) compared to simulated X-ray emission and absorption patterns for mono- ReO_3F , the structure identified by edge sharing octahedral units.



Figure S15: Experimental data (red) compared to simulated X-ray emission and absorption patterns for FReO₃ in which F occupies the perovskite A site and O moves to the X site.



Figure S16: Experimental data (red) compared to simulated X-ray emission and absorption patterns for tet-ReO₃ model in which all Re atoms migrate to a tetrahedral configuration.

Hard X-ray Photoelectron Spectroscopy HAXPES measurements were used to track the Re oxidation state in samples of $F_x \text{ReO}_3$ at various states of charge.



Figure S17: The Re 4f photoemission was used in order to track changes in the Re oxidation state during fluorination. A doublet at 43 and 46 eV is indicative of Re^{6+} , while a doublet at 46 and 48 eV is characteristic of Re^{7+} . Charging is seen to result in the growth of the peak at 48 eV, indicating partial oxidation of Re in F_x ReO₃.

Neutron Pair Distribution Function Analysis

Several different structural motifs were explored to account for the changes observed in the neutron pair distribution function (NPDF) upon fluoride insertion. As can be seen in Fig. S18, the data for pristine ReO₃ is in excellent agreement with the structural model. The pattern for $F_{0.6}$ ReO₃ is significantly more complicated, and attempts to fit the data have been unsuccessful. Instead, we have calculated the patterns for different structural models and compared them to the raw data. In this example, the *atom-atom* pair interactions were calculated from a hypothetical cell generated by making a 2 × 2 × 2 supercell of ReO₃, inserting fluoride to half of the perovskite *A*-sites (approx. $F_{0.6}$), and translating half of the rhenium atoms from octahedral sites toward the inserted fluorides, thus generating tetrahedral ReO₃F coordination sites. As can be seen, this correctly models the most significant features of the NPDF—such as the splitting of the first Re–X coordination sphere (1.87 Å to 1.73 and 1.90 Å)—but does not adequately capture the splitting observed in the X–X nearest neighbor distances around 2.47 and 2.68 Å.



Figure S18: Fit of NPDF data for pristine ReO_3 and comparisons of different calculated *atom-atom* pair interactions with $F_{0.6}\text{ReO}_3$.

Figures S19–S22 show several different structural motifs explored to try to explain the structural changes that occurred upon fluoride insertion. Several of them can account for some of the features observed in the data, but none of them can completely account for what is observed.



Figure S19: Comparison of observed data (black dots) for $F_{0.6}ReO_3$ versus the seven coordinate model.



Figure S20: Comparison of observed data (black dots) for $F_{0.6}ReO_3$ versus the Mono-ReO₃F model.



Figure S21: Comparison of observed data (black dots) for $F_{0.6}ReO_3$ versus the tetrahedral only ReO_3F model.



Figure S22: Comparison of observed data (black dots) for $F_{0.6}ReO_3$ versus the FReO₃ model (fluoride at the perovskite A-site).

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