



Cite this: *Chem. Commun.*, 2024,
60, 14589

Received 24th August 2024,
Accepted 28th October 2024

DOI: 10.1039/d4cc04331f

rsc.li/chemcomm

Interphase formation *versus* fluoride-ion insertion in tunnel-structured transition metal antimonites†

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Fluoridating reagents are used to model interfacial reactions in fluoride-ion batteries. Topochemical F-ion insertion is seen for one-dimensional (1D) tunnel-structured FeSb_2O_4 but interphase formation comprising antimony (oxy)fluorides is observed for MnSb_2O_4 .

Grid-level energy storage requires a diversity of battery chemistries so as to alleviate stresses on current mineral supply chains and to provide safer alternatives to Li-ion batteries.^{1–3} “Beyond Li” alternatives such as Na-ion batteries are yet to realize comparable energy densities, and often do little to diversify materials palettes.^{4,5} Fluoride-ion batteries, which implement fluoride anions as charge carriers have received considerable attention as an orthogonal alternative with the potential to alleviate supply chain challenges and preclude the need for metal electrodeposition.^{6–10} Fluoride conversion electrodes have shown promise but challenges remain with regards to high temperatures for successful operation, large volume changes, and sluggish fluoride-ion diffusion.^{6–8} Much recent attention has focused on the design of insertion-based fluoride electrode materials where the integrity of the structural framework of insertion electrodes is preserved upon F-ion insertion/deinsertion.¹¹ However, a key consideration is the competition between ion insertion and interphase formation.¹² Here, we use fluoridating reagents, XeF₂ and NOBF₄, as models for interfacial electrode reactions to contrast F-ion reactivity in 1D tunnel-structured FeSb₂O₄ and MnSb₂O₄, which both adopt the schafarzikite-type structure but with distinctive oxidation potentials (0.771 and 1.56 vs. standard hydrogen electrode (SHE) for Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺, respectively).¹³ We utilize a broad suite of spectroscopic methods to probe chemical reactivity in model F-ion

insertion hosts to differentiate between interphase formation and insertion reactions.

The schafarzikite-type MA_2O_4 structure sketched in Fig. 1 (M = transition metal, A = p-block element with stereochemically active lone pairs) forms 1D tunnels defined by corner-shared

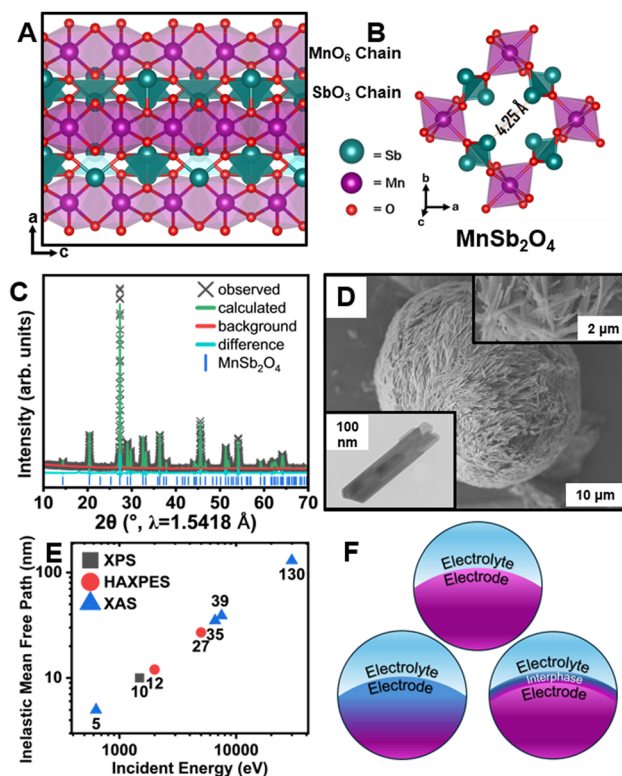


Fig. 1 Structure and characterization of MnSb_2O_4 . (A) Schafarzikite-type MnSb_2O_4 viewed along (010); (B) 1D tunnel of MnSb_2O_4 viewed along the c direction. (C) Rietveld-refinement to powder XRD pattern used to obtain the structures in (A) and (B). (D) SEM image of MnSb_2O_4 nanorods; top inset shows magnified SEM; bottom inset shows a TEM image. (E) IMFP of an electron calculated based upon the incident energy for XPS, HAXPES, and XAS measurements. (F) Schematic illustration of F-ion reactivity.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4cc04331f>

X-ray absorption near-edge structure (XANES) spectroscopy measurements of the as-prepared and fluoridated MnSb_2O_4 are shown in Fig. 2. Soft X-ray (surface sensitive) Mn L-edge ($2p-3d$) spectra for XeF_2 -treated MnSb_2O_4 are plotted in Fig. 2A. Corresponding Fe L-edge data for XeF_2 -reacted FeSb_2O_4 are plotted in Fig. 2B. In contrast to FeSb_2O_4 , where F-ion insertion brings about oxidation of the Fe center,^{14,15} the Mn L₃-edge spectra with a pronounced absorption at 640 eV characteristic of divalent Mn do not evidence signatures of Mn oxidation upon treatment with XeF_2 .²³ As such, both powder XRD and Mn L-edge XANES measurements do not support the notion of F-ion insertion. However, Fig. 2C shows that reaction of MnSb_2O_4 results in the emergence of the F K-edge ($1s-2p$), characteristic of fluoride moieties at the surface. This and the EDS measurements

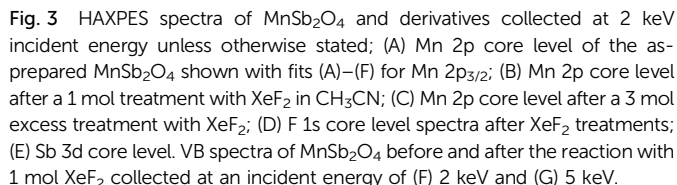
Figure 1 displays X-ray Photoelectron Spectroscopy (XPS) spectra for Mn, Fe, and Sb in MnSb₂O₄ and FeSb₂O₄. The figure is organized into two rows of five panels each, labeled A through J.

Top Row (A-E): Shows the intensity (arb. units) versus Incident Photon Energy (eV) for Mn L₃, Fe L₃, F K, Mn K, and Fe K core levels. The spectra are recorded for MnSb₂O₄ (black line) and FeSb₂O₄ (blue line) samples, and for samples annealed in 1:1 XeF₂ at 55°C (green line) and 75°C (red line), and in 1:5 XeF₂ at 25°C (blue line).

Bottom Row (F-J): Shows the first derivative of the intensity (arb. units) versus Incident Photon Energy (eV) for Mn K, Fe K, O K, Sb M₄, and Sb K core levels. The spectra are recorded for MnSb₂O₄ (black line) and FeSb₂O₄ (blue line) samples, and for samples annealed in 1:1 XeF₂ at 55°C (green line) and 75°C (red line), and in 1:5 XeF₂ at 25°C (blue line).

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To probe the electronic structure of MnSb_2O_4 before and after XeF_2 treatment, valence band (VB) spectra were acquired using energy-variant HAXPES (Fig. 3E and F). The photoionization cross-sections of orbitals have an incident energy-dependent decay that can be utilized to decipher orbital contributions.^{14,22} Orbital subshells with higher orbital angular momentum (*e.g.*, d and f shells) contribute greater intensity to the VB spectrum at lower incident energies. In contrast, at higher energies, the s and p shells make a greater contribution to the VB.¹⁴ A subtle diminution in intensity is visible for fluoridated MnSb_2O_4 at



The most significant change in HAXPES spectra is observed in the F 1s region (Fig. 3D). Treatment with a 1 : 1 molar ratio of XeF₂ yields a singular F 1s feature, but upon treatment with a 3-molar excess of XeF₂, a second F 1s feature is observed. The

interstitial sites along its tunnel, the latter is characterized by very limited bulk F-insertion. The insertion of fluoride-ions is instead constrained by the formation of an interphase layer on the surfaces of the MnSb_2O_4 particles. While Mn affords a higher oxidation potential, the overlap of Mn 3d-derived states with Sb states at the valence band edge promotes the preferential formation of amorphous antimony fluoride or antimony oxyfluoride interphasic products. Understanding the reactivity of model systems will assist in the future realization of viable F-ion insertion electrodes and full batteries.

Fig. S10 (ESI[†]) plots a Mn L₃-edge XANES spectrum acquired for MnSb₂O₄ after treatment with NOBF₄. The spectrum shows a slight shift of the white line absorption and diminution of the pre-edge feature at 639 eV. Fig. S11 (ESI[†]) shows Sb M₄-edge and O K-edge XANES spectra for the as-prepared MnSb₂O₄ and after treatment with a 3-molar excess of NOBF₄. Similar to Fig. 2B, no shift of the white line absorption energy is observed, which indicates retention of a nominally trivalent oxidation state for Sb. However, a pronounced modification of relative intensities of features centred at 531 eV and 536 eV is suggestive of a change in the Sb local coordination environment. F K-edge XANES spectra in Fig. S11B (ESI[†]) indicate the presence of anionic fluoride species after NOBF₄ treatment. Core-level HAXPES spectra (Fig. S11B–D, ESI[†]) show pronounced changes suggestive of the accumulation of an interphasic product. The O 1s core level is significantly decreased in intensity as compared to overlapping Sb 3d states, indicating that there is less oxygen on the surface (Fig. S11C, ESI[†]). The shift in binding energy for the Sb 3d_{3/2} core level further suggests an alteration of the surficial Sb local coordination environment. Based on these observations, the interphase layer is most-likely formed by amorphous antimony fluorides and oxyfluorides, such as SbF₃ or a F-rich oxyfluoride such as Sb₃O₂F₅ (Fig. S11E–G, ESI[†]). Table S4 (ESI[†]) provides balanced chemical equations for the formation of each of these species. While NOBF₄ is a stronger oxidizing reagent, based on the electronic structure considerations depicted in Fig. S5 (ESI[†]), it promotes increased antimony oxidation and exacerbates the formation of the interphasic product. Fig. S12 (ESI[†]) depicts crystal structures of the candidate materials but based on X-ray scattering, the interphasic products do not appear to have long-range order.

Understanding the competitive nature of insertion *versus* interphase formation is key to the design and discovery of insertion electrodes of fluoride-ion batteries. We find a sharp contrast between low-dimensional FeSb_2O_4 and MnSb_2O_4 , both of which crystallize in a schafarzikite-type structure with a 1D tunnel. While the former reversibly accommodates F-ions in

The data supporting this article have been included as part of the ESI.†

The authors have no conflicts of interest to declare.

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