Supplementary Information

Capacity enhancement of $LaAl_2Ag$ ternary alloy anode for fluoride-ion batteries

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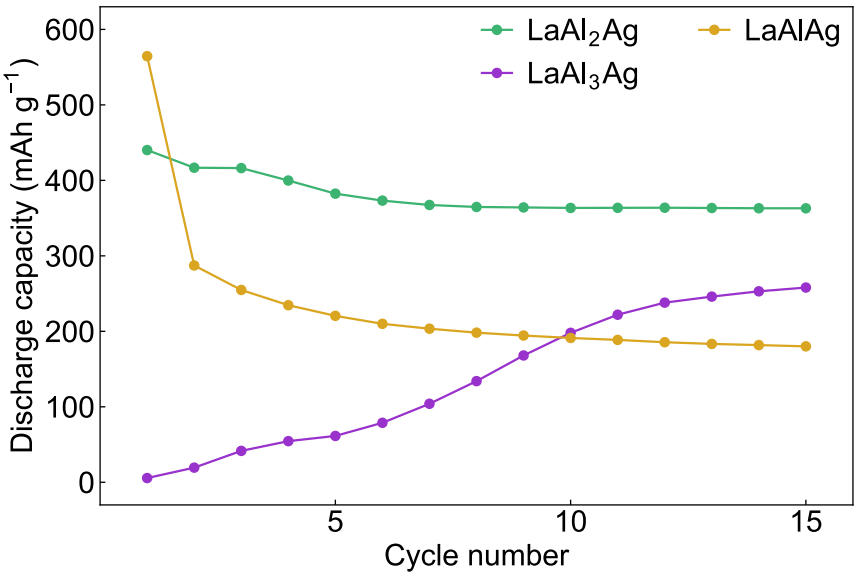

Fig. S1 Comparison of discharge capacities between LaAlAg, $LaAl_2Ag$, and $LaAl_3Ag$ anodes.

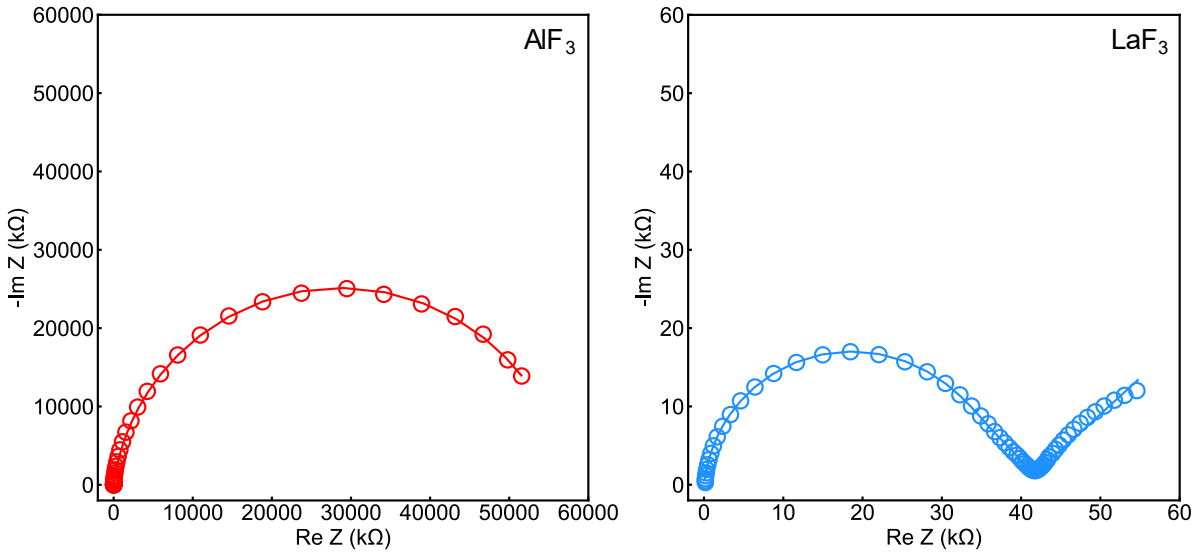

Fig. S2 Electrochemical impedance spectra obtained from AlF_3 and LaF_3 at 140℃ (colored circles: experimental data, solid lines: fittng data). The F^- ion conductivities of AlF_3 and LaF_3 are determined to be $(1.08 \pm 0.03) \times 10^{-9}$ and $(1.79 \pm 0.06) \times 10^{-6}$, respectively.

Note S1. To investigate the phase evolution of the whole part of $LaAl_2Ag$ anode during cycling, we acquired XRD patterns from the $LaAl_2Ag$ anode composites in the pristine, discharged, and charged states, respectively, as shown in Fig. S3. Since the anode composite contains a large amount of $La_{0.9}Ba_{0.1}F_{2.9}$ (LBF) solid electrolyte, we found unchanged strong Bragg peaks of LBF in all the XRD patterns, as marked by asterisk symbols (*). We also found unchanged minor peaks of an impurity phase (marked by #), which could be derived from a partial decomposition of LBF solid electrolyte from the tysonite phase into the fluorite phase. From the XRD patterns in the pristine state, $LaAl_2Ag$ is identified to be multiple phases consisting of $LaAl_{3.4}Ag_{0.6}$ (ICSD #402575), LaAg (ICSD #58288), and $AlAg_2$ (ICSD #107717). Although the intensities of XRD peaks of $LaAl_{3.4}Ag_{0.6}$ and LaAg phases are reduced from the pristine to the discharged states, we still find these peaks in the discharged and charged states, as indicated by the blue and purple triangles. This result suggests that the original $LaAl_2Ag$ alloy is partially fluorinated in the initial cycling, which is well consistent with the result of the discharge/charge test in Fig. 1a. On the basis of STEM observations, LaF_3, AlF_3, and Ag nanocrystals are formed in the discharged state, and AlF_3 is solely defluorinated to Al in the charged state. However, the strong XRD peaks of LBF largely overlap with those peaks of LaF_3, AlF_3, Ag, and Al, and it becomes difficult to clearly distinguish their peaks, as indicated by the green, orange, pink, and red squares.

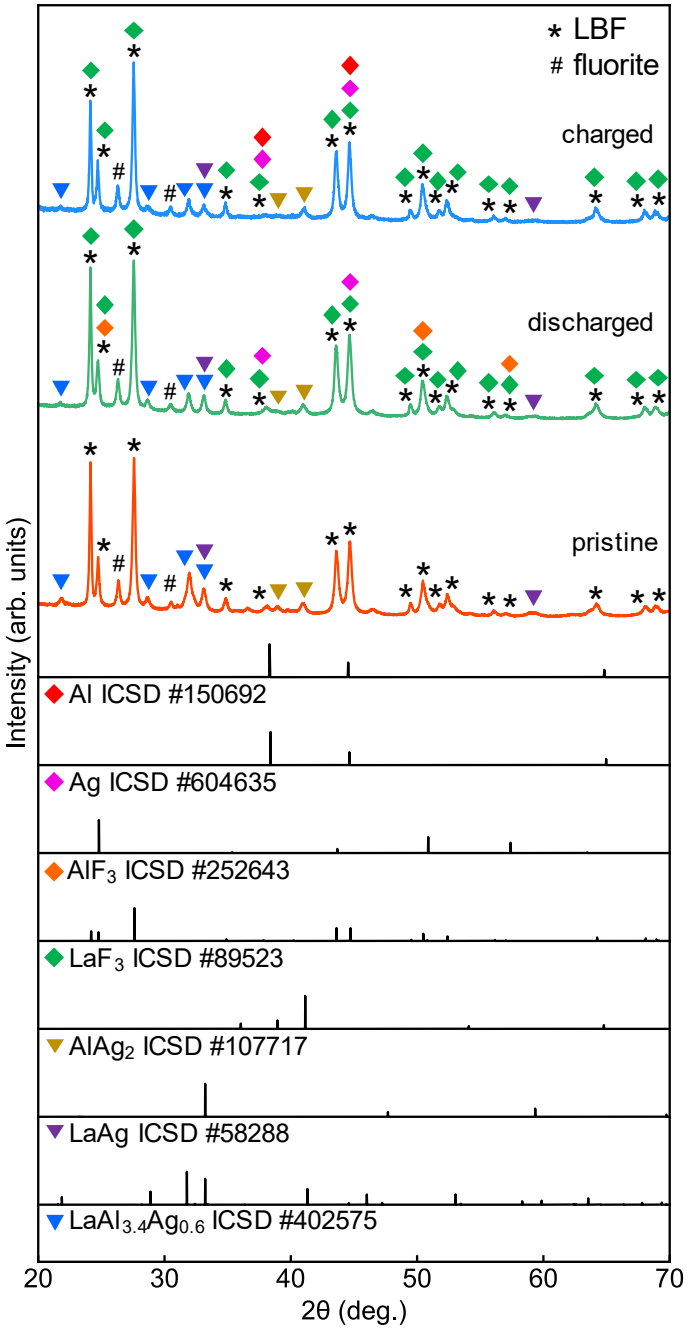

Fig. S3 Powder XRD patterns obtained from the anode composites in the pristine, discharged, and charged states, respectively.