Supporting Information

Batteries based on fluoride shuttle

M. Anji Reddy and M. Fichtner*

Synthesis of materials:

All sample preparations, assembly and testing of the cells was done under an inert gas atmosphere in an argon filled glove box with recirculation. The fluoride samples were dried under vacuum at appropriate temperatures. Electrolyte and cathode materials were prepared by high energy ball milling using sealed silicon nitride vials and balls. The ball to sample weight ratio was 12:1. In the case of electrolyte stoichiometric amounts of LaF_3 and BaF_2 were milled at 600 rpm for 12h. For the preparation of electrode materials first LaF_3 and BaF_2 were mixed and milled for 4h at 600 rpm then the active materials CuF_2 and carbon were added to the electrolyte mixture in appropriate ratios and milled further for 12h at 600 rpm.

In case of BiF_3 two types of conditions were used. One BiF_3 electrode material was prepared similar to CuF_2 composite. The material obtained under these conditions is called BiF_3 solid solution electrode. In another case BiF_3 and carbon was mixed and milled at 600 rpm for 12h. Then this composite was mixed with electrolyte in appropriate ratio and milled at 150 rpm for 12h. The material obtained under these conditions is called BiF_3 composite electrode. In case of $KBiF_4$ stoichiometric amounts of KF and BiF_3 and carbon were milled for 12h at 600 rpm. Similarly SnF_2 and carbon were mixed and milled at 600 rpm for 12h. Cerium metal received from Aldrich was used as anode.

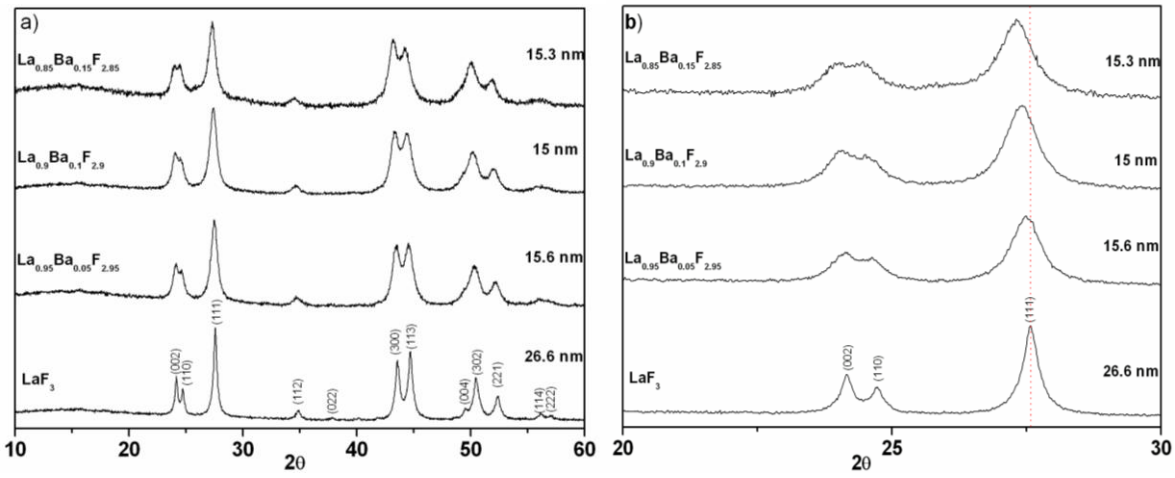

Figure S1. XRD patterns of $La_{1-x}Ba_xF_{3-x}$ ($0 \leq x \leq 0.15$) samples synthesized by mechanical milling

Electrochemical studies:

For electrochemical studies weighed amounts of Ce+$La_{0.9}Ba_{0.1}F_{2.9}$+Cathode composite were pressed together into 7 mm diameter pellets using a PerkinElmer hand press. The total thickness of the pellet was ~ 1 mm. Typical thickness of the anode, electrolyte and cathode layers were 120 µm, 750 µm and 30 µm respectively as determined from cross-sectional SEM studies. The mass of the cathode material was 4-5 mg. Table S1 shows the composition of the electrodes used in this study; Figure S2 shows the schematic drawing of a pellet. The pellets were placed in modified Swagelok cells and tightened inside the argon filled glove box. The Swagelok cells were heated using a temperature programmed band heater.

Table S1 composition of the electrodes used in this study; the numbers in the parenthesis indicate the weight ratios of the materials that are present in the electrode.

Cathode	Electrolyte	Anode
CuF_2 + $La_{0.9}Ba_{0.1}F_{2.9}$ +C (30 + 60 + 10)	$La_{0.9}Ba_{0.1}F_{2.9}$	Ce metal
BiF_3 + $La_{0.9}Ba_{0.1}F_{2.9}$ + C (30 + 60 + 10) Composite electrode	$La_{0.9}Ba_{0.1}F_{2.9}$	Ce metal
BiF_3+ $La_{0.9}Ba_{0.1}F_{2.9}$ + C (30 + 60 + 10) Soli solution electrode	$La_{0.9}Ba_{0.1}F_{2.9}$	Ce metal
$KBiF_4$ + C (90 + 10)	$La_{0.9}Ba_{0.1}F_{2.9}$	Ce metal
SnF_2 + C (90+10)	$La_{0.9}Ba_{0.1}F_{2.9}$	Ce metal

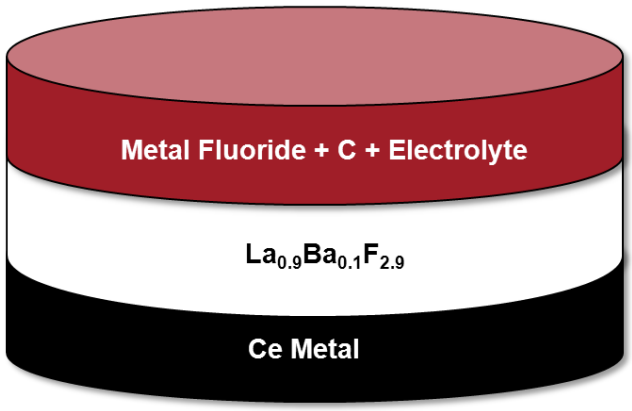

Figure S2: Figure: Architecture of the samples tested in this study