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### **IT-7-P-3047 Reversible In-Situ TEM Electrochemical studies of Fluoride Ion Battery**

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New research directions in Li-ion batteries are focusing on improvements of battery performance. Alternative technologies are investigated based on different chemistries using, e.g., sodium, magnesium or chloride as charge transfer ions in secondary batteries. Batteries based on a fluoride ion shuttle (fluoride ion battery) are an interesting alternative to Li-ion batteries as they can theoretically provide substantially higher volumetric energy densities compared to Li-ion batteries. Recently, the principle of a secondary battery based on a fluoride ion shuttle has been demonstrated [1]. Here, the electrolyte is one of the key components to obtain good cycling properties (e.g., resulting from fast F<sup>-</sup> conduction in fluoride ion batteries)[2].

For performing in-situ electrochemical studies, the stability of the components towards the electron beam (with beam energy and beam current being critical parameters) is essential to clearly interpret the results for the battery system in terms of the electrochemical performance. In the case of the F<sup>-</sup> batteries, the components besides being stable under the electron beam do not require an inert transfer, thus being suited as a good model system for in-situ electrochemical studies inside the TEM.

Ball milling of a mixture of (1-y)LaF<sub>3</sub> and yBaF<sub>2</sub> was employed to prepare La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>. Initially, the electrolyte (La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub>) was studied for its structure, composition, porosity and stability under the electron beam. The cathode material based on a mixture of Bi (active material), La<sub>0.9</sub>Ba<sub>0.1</sub>F<sub>2.9</sub> (ionic conductivity) and C (electronic conductivity) was prepared. Both materials were pressed to form a pellet. A lamellae of 60X35µm was prepared and electrically contacted on the Aduro Electrochemical device (E-AEK11 from Protochips Inc.) inside the focused ion beam system (FEI Strata 400S). An Aduro sample holder from Protochips Inc. along with a Keithley 2611 sourcemeter in the FEI Titan 80-300 TEM were used in this work. SAED and HRTEM studies indicated the formation of a BiF<sub>3</sub> phase in the cathode (reflections corresponding to d-values of 5.85Å(100)<sub>BiF<sub>3</sub></sub> and 3.37Å(111)<sub>BiF<sub>3</sub></sub>, which were absent in the as-prepared state). The electrolyte structure at the interface to the cathode also changed during charging, where reflections corresponding to La were observed, indicating local reactions in the electrolyte leading to the formation of a La/LaBaF<sub>3</sub>/BiF<sub>3</sub> cell. During discharging, most of the BiF<sub>3</sub> was again reduced indicating the reversible behavior of the battery system in the TEM.

[1] M. Anji Reddy, M. Fichtner, J. Mater. Chem 21 (2011), p17059.

[2] C. Rongeat, M. Anji Reddy, R. Witter, et.al., ACS Applied Materials and Interfaces, 6 (2014) p2103.

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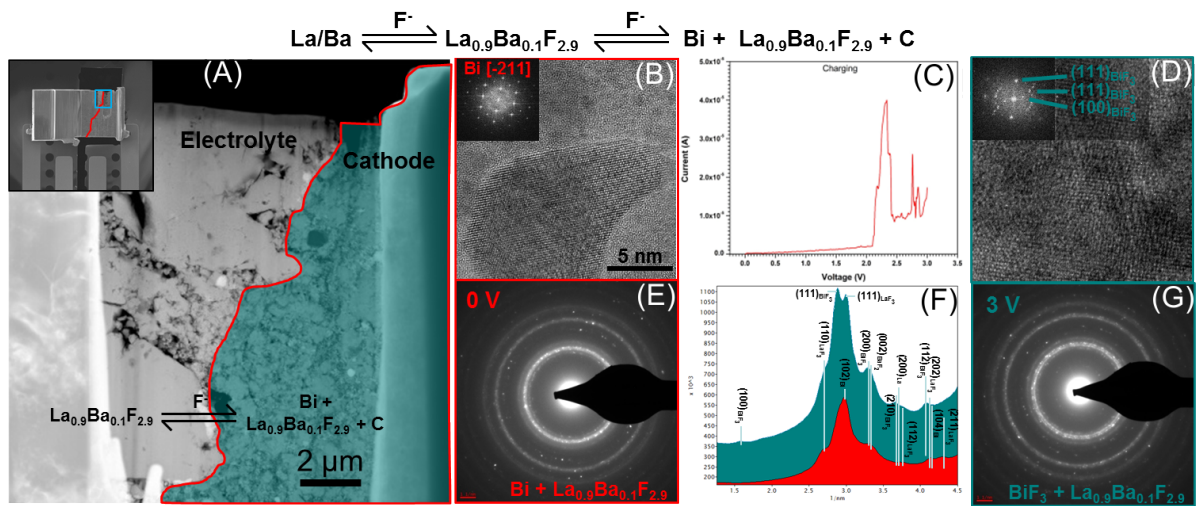


Fig. 1: (A) Thin lamella on MEMS device through FIB preparation. HRTEM micrograph and SAED pattern of cathode (B),(E) at 0V and (D),(G) at 3V respectively. (C) I-V curve during charging. (F) Line profiles of diffraction patterns showing intensive peaks of Bi and  $\text{BaF}_3$  cleaving at 3V, as evidence of structural change in the electrode, through formation of  $\text{BiF}_3$ .