

## Reversible In-Situ TEM Electrochemical studies of Fluoride Ion Battery

Venkata Sai Kiran Chakravadhanula<sup>1</sup>, Mohammed Hammad Fawey<sup>2</sup> and Christian Kuebel<sup>1,2,3</sup>, Torsten Scherer<sup>2,3</sup>, Carine Rongeat<sup>2</sup>, Anji Reddy Munnangi<sup>1,2</sup>, Maximilian Fichtner<sup>2</sup>, Horst Hahn<sup>1,2</sup>

<sup>1</sup>. Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Albert-Einstein-Allee 11, 89081 Ulm, Germany.

<sup>2</sup>. Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

<sup>3</sup>. Karlsruhe Institute of Technology, Karlsruhe Nano Micro Facility (KNMF), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

In addition to further developments in Li-ion batteries, new research directions are focusing on further improvements of the 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].

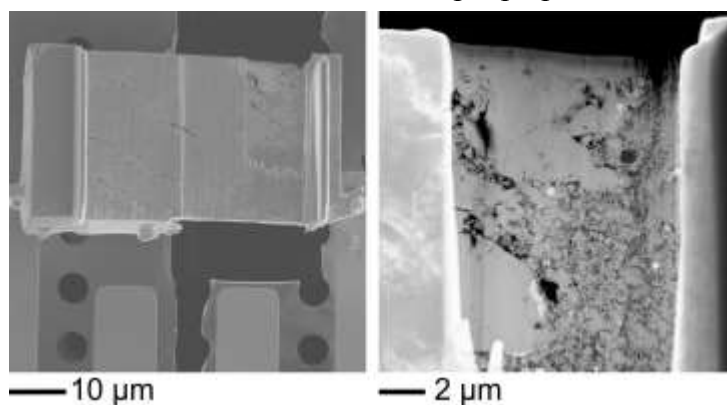
For performing in-situ electrochemical studies, the stability of the electrodes and electrolytes towards the electron beam (with beam energy and beam current being critical parameters) is essential to clearly interpret the results for the battery system in terms of the electrochemical performance. Furthermore, the necessity for inert transfer of the solid state battery into the electron microscope is typically a limiting factor for most studies on lithium-based batteries. In the case of the fluoride ion batteries, the electrodes and electrolyte 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 y BaF<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>) has been 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> (for ionic conductivity) and C (for electronic conductivity) was prepared. Both electrolyte and cathode material were pressed to form a pellet. From this pellet lamellae of 60 urn X 35 urn were prepared inside the focused ion beam system (FEI Strata 400S) for the in-situ measurements. An omniprobe 200 micromanipulator was used to place the lamellae on the Aduro Electrochemical device (E-AEK11 from Protochips Inc.) and to electrically contact the selected structures on the sample using a Pt GIS system. An Aduro single tilt sample holder from Protochips Inc. has been used to carry out the in-situ measurements using a Keithley 2611 source meter in the FEI Titan 80-300 aberration corrected transmission electron microscope. The studies were performed in diffraction mode, formation of a BiF<sub>3</sub> phase were observed in selected area diffraction studies of 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). Surprisingly, the electrolyte structure at the interface to the cathode also changed during charging, where reflections corresponding to La were observed, which were not present initially, indicating local reactions in the electrolyte leading to the formation of a La/LaBaF<sub>3</sub>/BiF<sub>3</sub> cell. After discharging, most of the BiF<sub>3</sub> was again reduced indicating the reversible behavior of the battery system in the TEM.

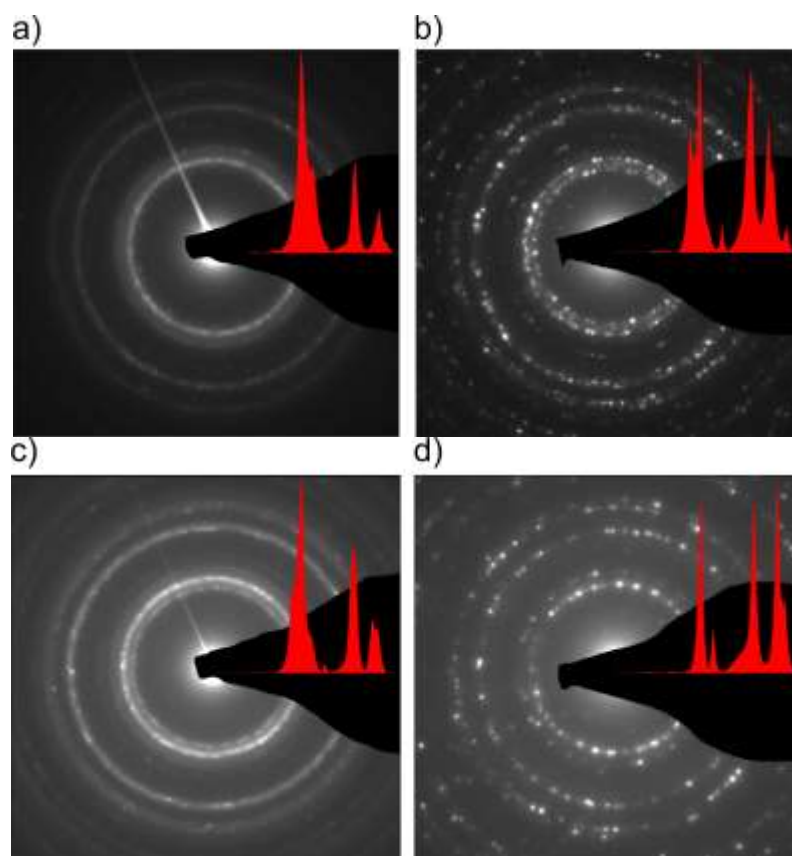
[1] M. Anji Reddy, M. Fichtner, *J. Mater. Chem* **21** (2011), p17059.

[2] C. Rongeat, M. Anji Reddy, R. Witter, et.al., *ACS Applied Materials and Interfaces*, Article ASAP

[3] The authors acknowledge support from the Karlsruhe Nano Micro Facility (KNMF). Robby Prang is acknowledged for his useful discussions towards the sample preparation in this work.



**Figure 1.** (Left) SEM image depicting the geometry of the lamella placed on the Aduro Electrochemical device (E-AEK11) and (Right) HAADF-STEM image showing the interface between electrolyte and cathode.



**Figure 2.** SAED patterns from the same region of the electrode (a) before, (b) at 3.3 V during biasing, the electrolyte (c) initially and (d) at 3.3 V during biasing inside the electron microscope.