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Title of dissertation	<i>In situ</i> and <i>Ex situ</i> TEM Studies of Fluoride Ion Batteries
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Abstract

Lithium ion batteries (LIBs) are widely used for portable electronics. However, their application is limited because of energy density, safety issues, and the high cost. This necessitates a search for alternative battery technologies. Many alternative battery systems are currently investigated based on different chemistries, which include sodium, magnesium, chloride, aluminum, and potassium based batteries. Rechargeable batteries based on a fluoride anion shuttle are a promising alternative to Li-ion batteries with theoretical energy densities of more than 5000 WhL⁻¹. However, detailed chemical and structural investigations are necessary to understand the structural changes and the degradation mechanisms to improve the performance of fluoride ion batteries. In the present thesis, TEM has been used to study all-solid-state fluoride ion batteries *in situ* and *ex situ*.

For *in situ* TEM studies, two all-solid-state fluoride ion battery systems were used; a half-cell consisting of a Bi composite as electrode and La_{0.9}Ba_{0.1}F_{2.9} as a solid electrolyte; and a full cell consisting of a Cu composite as cathode, a MgF₂ composite as anode, and La_{0.9}Ba_{0.1}F_{2.9} as a solid electrolyte. Optimization of sample preparation was an essential step to enable reliable *in situ* TEM studies during electrochemical biasing. Challenges during sample preparation, such as re-deposition/metal contamination, contact resistance, porosity of the battery materials and leakage current were resolved using an optimized FIB based approach. The successful preparation has been demonstrated for two fluoride ion battery systems. The *in situ* TEM studies of the half-cell revealed the fluorination of Bi and Bi₂O₃ forming BiF₃ and BiO_{0.1}F_{2.8}, and the simultaneous reduction of La_{0.9}Ba_{0.1}F_{2.9} to La and Ba during charging. During discharging, most of the BiF₃ was reduced to Bi metal. Comparing the structural changes with the electrochemical

charging curve, the main phase formed was the irreversible phase $\text{BiO}_{0.1}\text{F}_{2.8}$, leading to the poor reversibility of the half-cell. On the other hand, the TEM studies of the cathode-electrolyte interface of the full cell revealed fluoride migration into the composite cathode during charging resulting in the formation of CuF_2 , which was absent in the as-prepared state. Due to the high volumetric changes associated with the CuF_2 formation, the cell fractured at the cathode-electrolyte interface during the second charging. However, a detailed electrochemical study during discharging was problematic, as a short circuit between cathode and anode dominated the current.

In addition, a fluoride ion battery system consisting of a CuF_2 composite as cathode, $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$ as a solid electrolyte, and a La sheet as anode was studied *ex situ* in the as-prepared, discharged, and recharged states. The interfacial studies were performed by lifting-out two lamellae from each pellet at the electrodes-electrolyte interfaces using FIB. The TEM studies of the cathode confirmed the defluorination/fluorination during cycling of CuF_2/Cu . However, the TEM studies revealed a high oxygen content in the cathode composite explaining the difference between the theoretical capacity of Cu/CuF_2 (528 mAh g^{-1}) and the observed capacity during the first discharge (360 mAh g^{-1}). On the anode side, the presence of La_2O_3 on the surface led to a side reaction by LaOF formation during recharging, which acts as a significant fluoride trap. Therefore, the capacity faded upon cycling to only 165 mAh g^{-1} in the second discharge. Moreover, The STEM-EDX maps revealed Cu diffusion from the cathode into the electrolyte due to the high volumetric change in the cathode, partially explain the capacity fading.