

## STRUCTURE EVOLUTIONS AND MECHANICS OF MATERIALS DURING ELECTROCHEMICAL ION INSERTION

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### Abstract

Electrochemical ion insertion plays an important role in secondary batteries like lithium ion batteries and sodium ion batteries. Electrochemical ion insertion involves coupled ion-electron transfer and usually causes crystal/electronic structure changes as well as chemical stress/strain of the host materials. This presentation discusses the crystal and electronic structure evolution of CeO<sub>2</sub>, MoS<sub>2</sub>, and RuO<sub>2</sub> during electrochemical lithium/sodium ion insertion, and the chemical strain of graphite during lithium ion insertion. The electrochemical lithium insertion as an effective method to improve the electrocatalytic performance of RuO<sub>2</sub> will also be introduced.

### 1. Introduction

Structural evolutions are often observed during lithium/sodium insertion/extraction and are highly relevant to the thermodynamics, kinetics, and numerous performance metrics of materials. For example, a first-order phase transition occurs in ion-insertion materials to store energy reversibly such as LiFePO<sub>4</sub> and TiO<sub>2</sub> with formation of a distinct new structural phase. Or sometimes, the ion insertion may not involve with crystal structural changes, but with obvious electronic structure changes and lattice expansion/distortion. This kind of structural evolution often endows the host materials with interesting properties. In addition, the reversible insertion and extraction of ions into/from the materials result in periodical structural and volume changes, which is more or less like a cyclic loading applied on the host materials and results in material fatigue. Thus, an in-depth study of the structural evolutions and mechanics of the materials is of significance for not only improving their performance but also expanding their applications.

### 2. Results

The structure evolutions/mechanics of MoS<sub>2</sub>, CeO<sub>2</sub>, RuO<sub>2</sub>, and graphite during electrochemical lithium/sodium ion insertion were investigated and the findings were as described below:

- a. The phase transition and electrochemical performance of 2H-MoS<sub>2</sub> during sodiation in ether and ester electrolytes were studied (Fig.1a). Interestingly, we find that the MoS<sub>2</sub> anode develops MoS<sub>2</sub>/diglyme-Na<sup>+</sup> superlattices induced by co-intercalation of Na<sup>+</sup> and ether solvent in ether electrolyte, rather than the conversion reaction observed in ester electrolyte. The superlattices consist of mixed semi-conductive 2H and metallic 1T phases, and are structurally stable and kinetically favorable for the repeated sodiation, which greatly enhances the capacity, cycling, and rate performance of MoS<sub>2</sub>.
- b. A reversible first-order phase transition was discovered during (de)lithiation of CeO<sub>2</sub> nanoparticles (Fig.1b). The Li<sub>x</sub>CeO<sub>2</sub> compound phase is identified to possess the same fluorite crystal structure with FM3M space group as that of the pristine CeO<sub>2</sub> nanoparticles. The DFT calculations further reveal that the Li induced redistribution of electrons causes the increase in the Ce-O covalent bonding, the shuffling of Ce and O atoms, and the jump expansion of lattice constant, thereby resulting in the first-order phase transition.
- c. An electrochemical lithium intercalation method to improve both the activity and stability of RuO<sub>2</sub> for acidic oxygen evolution reaction (OER) was reported (Fig.1c). The lithium intercalates into the lattice interstices of RuO<sub>2</sub>, donates electrons and distorts the local structure. Therefore, the Ru valence state is lowered with formation of stable Li-O-Ru local structure, and the Ru-O covalency is weakened, which suppresses the dissolution of Ru, resulting in greatly enhanced durability. Meanwhile, the inherent lattice

strain results in the surface structural distortion of  $\text{Li}_x\text{RuO}_2$  and activates the dangling O atom near the Ru active site as a proton acceptor, which stabilizes the  $\text{OOH}^*$  and dramatically enhances the OER activity.

- d. A home-made in situ measurement device was used to characterize simultaneously chemical strain and nominal state of charge, especially residual chemical strain and residual nominal state of charge, in graphite-based electrodes at various temperatures (Fig.1d). The measurements indicate that raising the testing temperature from 20 °C to 60 °C decreases the chemical strain at the same nominal state of charge during cycling, while residual chemical strain and residual nominal state of charge increase with the increase of temperature. Furthermore, a novel electrochemical-mechanical model is developed to evaluate quantitatively the chemical strain caused by solid electrolyte interface (SEI) and the partial molar volume of Li in the SEI at different temperatures.

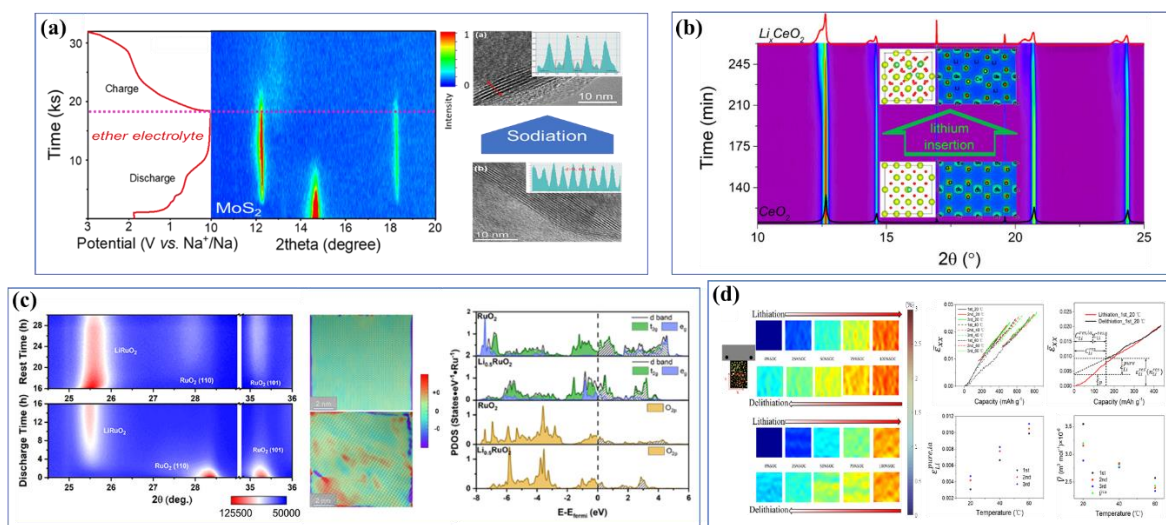


Fig.1 – (a) The phase transition of 2H-MoS<sub>2</sub> during sodiation in ether and ester electrolytes; (b) The structural evolution of CeO<sub>2</sub> during lithiation; (c) The structural evolution of RuO<sub>2</sub> during lithiation; (d) The chemical strain of graphite during lithiation.

### 3. Conclusions

The electrochemical lithium/sodium insertion into MoS<sub>2</sub>, CeO<sub>2</sub> and RuO<sub>2</sub> induces first-order phase transitions. Specifically, a MoS<sub>2</sub>/diglyme-Na<sup>+</sup> superlattice forms in MoS<sub>2</sub>. The phase transition of CeO<sub>2</sub> and RuO<sub>2</sub> is accompanied with distinct electronic structure changes of the metal cations, inspiring their applications in electrocatalysis. The chemical strain of graphite during lithiation is dependent on the Li concentration and ambient temperature.

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