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In situ Investigation of Nanoelectrochemical Systems

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***Abstract* — We report an *in situ* experimental characterization method of nanoelectrochemical systems (NECSs). Experiments were performed using nanorobotic manipulation inside a transmission electron microscope together with an electrochemical work station. The electrochemical behavior of an Mg-MgO-MoS_2 hetero-structure demonstrated the potential application of Mg as an anode for an ion-battery. Due to the abundant amount of magnesium on the earth, the investigation promises a low-cost anode material for a new generation of batteries. The application of 2D layered MoS_2 crystals also provides a solution of using layered nanostructures as high-capacity cathodes. Several key techniques for *in situ* nanoelectrochemical investigations were also presented in this report.**

Index Terms* – *In situ nanotechnology, nanoelectrochemical systems, nanobattery

I. Introduction

In situ nanotechnology has been widely used in the manipulation, fabrication, assembly, and property characterization of a variety of nanomaterials and nanoscale electromechanical, fluidic, photonic, and thermal systems. The interest in introducing the *in situ* technology into the emerging nanoelectrochemical systems (NECSs) has been stimulated by the fast expanding interests in the development of ion-batteries. To achieve higher power density, longer cycling life, and safer operation condition [1-4], it is needed to understand the microscopic mechanisms of the ion migration and distribution during the charging and dis-charging processes [1-3, 5-8]. Nanorobotic manipulation, transmission electron microscopy (TEM), elementary analytical spectroscopy (e.g., energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS)), together with a chemical work station will enable *in situ* investigation of NECSs from both the fundamental and application aspects, providing the possibility to correlate the structural change of the anode/cathode materials to the ion transport properties.

II. Setup

We carried out *in situ* electrochemical experiment in an Mg-MgO-MoS_2 heterostructure by using the above mentioned techniques. The setup is schematically shown in Fig. 1.

There are two major areas for the nanoelectrochemical investigations: the development of the TEM holder that is specifically adaptable to the *in situ* nanobattery and the selection and testing of the different combinations of the positive electrode material and negative electrode materials that can provide higher coulombic efficiency and longer cycling time.

There are three requirements for the design of the TEM holder:

1. The holder should be equipped with I/O ports that can directly connect to an electrochemical work station,
2. The holder should be designed with sample slots that are suitable for both liquid and solid electrolytes, providing more choices for the nanobattery architectures, and
3. The holder should be equipped with a nanopositioner for nanorobotic manipulation, with which the anode/cathode tip can easily be coupled with the sample materials (electrolyte + cathode/anode), enabling the *in situ* charging/discharging of the nanobattery.

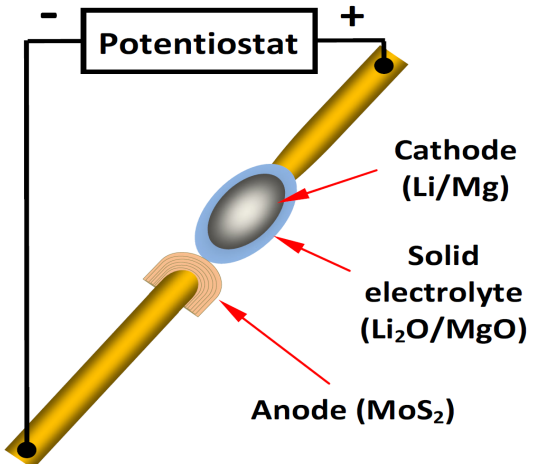

Fig. 1 Setup for the *in situ* electrochemical experiment.

III. Experiments and Future Works

Using the setup shown in Fig. 1, we have performed *in situ* experiments to understand the morphology change and ion migration during the charging/discharging processes (Figs. 2-4). The followings are anode/cathode materials to be tested:

1. For the cathode material, with the help of a nanomanipulator TEM holder, several active materials are possible, for example: metal magnesium or metal sodium;

2. Solid electrolytes are also a potential research area for the *in situ* nanobattery investigation;

3. 2D layered nanostructures, such as graphene or MoS_2 nanosheets, have the advantages of large storage capacity, long cycling time, and robust structures. Layered nanostructures as anode materials may accelerate the development of the ion battery.

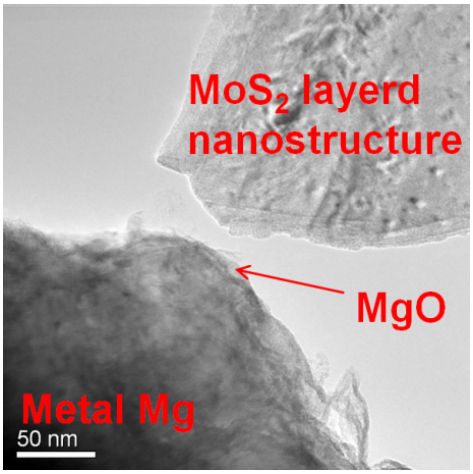

Fig.2 TEM observation of the Mg-MgO-MoS_2 charging/discharging experiment.

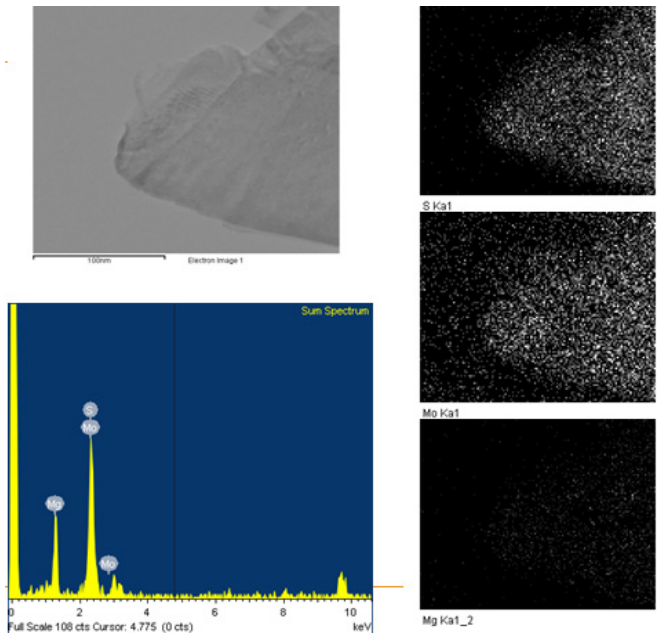

Fig.3 EDS and elemental mapping of the Mg-ion migration in the MoS_2 layered nanostructure during charging process.

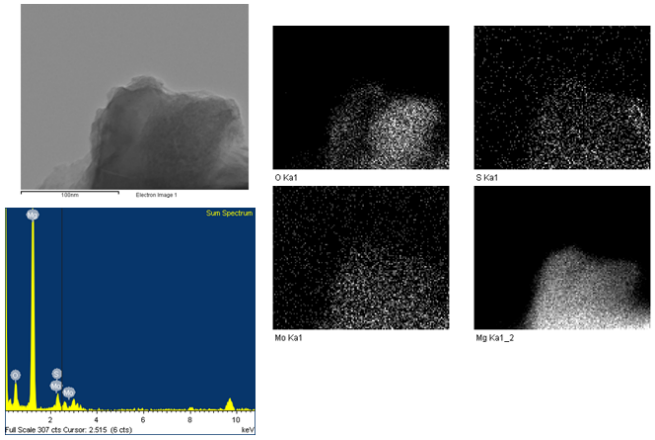

Fig.4 EDS and elemental mapping of the Mg-ion migration during the discharging process.

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