In Operando Monitoring of the Pore Dynamics in Ordered Mesoporous Electrode Materials by Small Angle X-Ray Scattering

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To monitor dynamic volume changes of electrode materials during electrochemical lithium storage and removal process is of utmost importance for developing high performance lithium storage materials. Small angle X-ray scattering (SAXS) is one of the most useful analytical techniques to investigate properties of nano materials since the SAXS technique works very well in characterizing unique nanostructures of materials with the probing range of 1 – 100 nm. In order to further gain insights on the nanostructural changes of materials during cycling, it is highly required to develop a new analytical technique with *in operando* capability to monitor physical changes of mesopores in the electrode material. We herein report an *in operando* probing of mesoscopic structural changes in ordered mesoporous electrode materials during cycling with synchrotron-based small angel X-ray scattering technique. *In operando* SAXS studies combined with electrochemical and other physical characterizations straightforwardly show how porous electrode materials underwent volume changes during the whole process of charge and discharge, with respect to their own reaction mechanism with lithium. Moreover, the changes of mesoscopic cell volumes upon lithiation and delithiation also can be exactly measured, from which we can get direct evidence that proves the role of mesopores in the active materials to effectively accommodate the volume expansion of crystalline frameworks by the reaction with lithium. Such a precise *in operando* probing technique for pore dynamics of ordered porous materials can be also utilized to study nanostructural changes of the electrode materials in other electrochemical systems adopting porous materials, such as electrode of the fuel cells, supercapacitor and metal-air battery systems. We also believe that *in operando* investigation of dynamic changes in the mesoscale order will help us to deeply understand physical behaviors of lithium storage materials, thereby providing valuable guidance for designing innovative nanostructured materials for next generation energy storage system.