

レドックス活性MOFの電気エネルギー貯蔵への応用

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【Abstract】 The development of cathode active materials of modern commercialized batteries has reached a bottleneck during last 5 years. One potential breakthrough may arise from the novel battery architectures and mechanisms that are brought by the discovery of new cathode active materials. Herein we designed metal-organic frameworks with multiple redox active sites, and applied them as the cathode active materials of Li-batteries. With electrochemical characterization and battery performance test, we have evaluated the potential of these MOFs being novel battery electrode materials. A series of operando physical measurements provided an insight to the redox active mechanism of these MOFs, and suggesting unprecedented electrochemical process that have never been observed in a conventional Li-ion battery. Therefore, these redox active MOFs are believed to bring inspirations for the material scientists, and suggesting fascinating architectures of next generation batteries.

【Introduction】 Electrical energy storage materials are considered preeminent alternatives to conventional fossil fuels due to their low cost, renewability and low environmental impact. Over the last decade, the evolution of materials has led to numerous innovations in the field. In the recent past, the Li-ion battery (LIB) is the pioneer technology as it provides both high energy density and large output current. The core cathode active materials conventionally used in the LIBs are layered metal oxides or metal salts, such as LiCoO₂ or LiFePO₄. The incomplete delithiation of their structure and the formation of insulating metal oxide layers at their interface⁷ have led to batteries with practical capacities much lower than their theoretical values, as well as degradation through large cycle numbers. As a substitute for metal oxides, organic-based materials have also been widely investigated and employed as cathode active materials. These materials are generally polymers with reversible redox active functional groups. With designable functional groups and flexible structures, these polymers lead to a tunable discharge voltage and ease of thin film fabrication and deposition on the electrodes, which permits an ultrafast charging speed. The drawbacks of organic-based materials are their self-discharge and low theoretical capacities, owing to their dissolution in electrolytes and large molecular weight per electron uptake. The preliminary results inspired us to develop advanced materials by combining the advantages of organic materials and molecular clusters. The practical strategy was to link the metal clusters with redox active organic bridging ligands to form porous coordination polymers (PCPs), which are also well known as metal-organic frameworks (MOFs). The potential of porous metal-organic frameworks (MOFs) of being elegant cathode active materials for lithium batteries. As crystalline materials, the outstanding structural stability of MOFs leads to a low risk of decomposition and explosion, which makes the MOFs favorable for the battery application.

[Methods] We selected anthraquinonedicarboxylic acid (H₂AQDC) as a bridging ligand. Anthraquinone (AQ) exhibits two reversible redox steps with one electron uptake for each. By combining these redox active ligands with the 3d transition metal ions, such as Mn and Cu, MOFs with redox active sites on both metal and bridging ligands can be achieved. A series of electrochemical analysis, such as cyclic voltammetry and battery performance test was performed on these redox active MOFs. Simple calculations will illustrate the electron uptake numbers of MOFs and therefore imply the valence change of metal and ligands. The mechanism could be further confirmed by the operando measurements, such as XANES and PXRD. With such result, we can achieve an insight of the electrochemical mechanism of these MOFs and comparing these mechanism with conventional batteries. Novel mechanisms may be observed in this process and provide the inspiration to the development of new materials.

[Results and Discussion]

The solvothermal reaction between 2,7-H₂AQDC and Cu(ClO₄)₂ · 6H₂O in N,N-dimethylformamide (DMF) led to the formation of a two-dimensional (2-D) metal organic framework with a formula of {Cu(2,7-AQDC)(DMF)}_∞. With the Mn²⁺ cations, a new redox active MOF with a formula of Mn₇(2,7-AQDC)₆(2,6-AQDC)(DMA)₆ is obtained. Using a lithium battery setup, cyclic voltammetry and battery performance analysis indicated that in both case the redox activity occurred on both metal clusters and bridging ligands. The reversible capacity of Cu-MOF and Mn-MOF were 105mAh/g and 200mAh/g respectively, which suggested a partial reduction of Cu-MOF and 100% redox activity of Mn-MOF. With *in situ* XANES measurements, a stepwise reduction of Cu₂(OAc)₄ was observed, in which the Cu(II) ions are reduced from a (II, II) state to (II, I) state and finally to a (I, I) state. In the case of Mn-MOF, the reversible Mn(II) to Mn(III) valence change was observed. Summarizing the electrochemical scheme, we realized that in the case of Mn-MOF, the oxidation of Mn(II) occurred and created extra positive charges on the framework, therefore the compensation for positive charges must be accomplished by adsorbing anions from the electrolyte. Such assumption was confirmed by *in situ* PXRD and *ex situ* solid state ¹⁹F-NMR. Finally, the sum up of the electrochemical scheme suggested a new mechanism of Li-batteries: both anions and Li-ions are independently inserted into MOFs and contribute to the total capacity. We name this mechanism as “bipolar charge”. This mechanism provides a potential strategy of electrochemical energy storage: put big ions in small pores may led to a combination of chemical and physical energy storage.

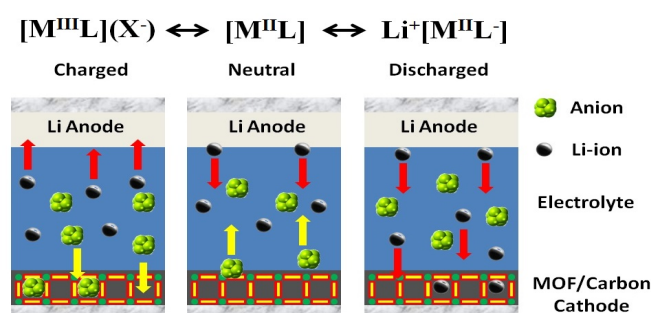


Fig. 1. A novel “bipolar charge” mechanism.

[References]

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