Redox Active Metal-Organic Frameworks (MOFs) as Novel Cathode Active Materials for Lithium Batteries

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ABSTRACT

The development of new materials for the energy storage purpose has been the mainstream research topic for the scientists in the last decade. In this vein, the active materials for lithium batteries and Li-ion batteries are of interest as they are portable energy storage devices with relatively large energy density, long life cycle and low environment impact. With the preliminary research, people have realized that besides the capacity and conductivity, the porosity and surface area of the materials are also critical factors which may significantly affect the operation speed and cycle stability of the battery. Such discovery suggested 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.

The known examples of MOF-based battery materials suffered from a low capacity issue that arises from the redox innocent ligands of these MOFs. A facile strategy to increase the total electron uptake capacity of the MOFs is to introduce redox active functional groups to the ligands. With this principle, our group synthesized two new metal-organic frameworks with 2,7-anthraquinone dicarboxylic acid (2,7-AQDC) and 2,6-anthraquinone dicarboxylic acid (2,6-AQDC), namely \{Cu(2,7-AQDC)(DMF)}\textsubscript{∞} and \{Mn\textsubscript{7}(2,7-AQDC)\textsubscript{6}(2,6-AQDC)(DMA)\textsubscript{6}\}\textsubscript{∞}. These MOFs exhibited redox activities on both metal clusters and anthraquinone ligands, which is evidenced by \textit{in situ} XANES measurement. The Cu-MOF possessed an initial capacity of 147mAh/g, but the capacity rapidly decreased within 20 cycles and stabilized at ~105mAh/g. The low efficiency of Cu-MOF may resulted by the insufficient Li-ion extraction during the charge process due to the poor conductivity and Li-ion diffusion rate in the Cu-MOF\textsuperscript{[1]}. Meanwhile, the Mn-MOF exhibited an initial capacity of 205mAh/g, which is significantly higher than the commercialized materials, such as LiCoO\textsubscript{2} and LiFePO\textsubscript{4} (~160mAh/g). The 50 cycle battery performance test indicated the Mn-MOF exhibited unprecedented recyclability while only ~5% capacity loss was observed within 50 cycles. With \textit{in situ} PXRD examination and solid state \textsuperscript{19}F-NMR result, we realized that a new mechanism for cathode active materials was illustrated in the case of Mn-MOF, in which the anions of electrolyte was intercalated into the framework during the charge process accompanied with Li-extraction. This mechanism reduced the ion intercalation number of MOF-materials and therefore increased the battery efficiency.

REFERENCES