Quinoid-Based Three-Dimensional Metal-Organic Framework, $Fe_2(dhbq)_3$: Porosity, Electrical Conductivity and Solid-State Redox Property

([1]*Graduate School of Science, Tohoku University*, [2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*) ○ Shraddha Gupta,[a]* Haruki Tanaka,[a] Kentaro Fuku,[a] Hiroaki Iguchi,[a] Ryota Sakamoto,[a] Hiroaki Kobayashi,[b] Yoshiyuki Gambe,[b] Itaru Honma, [b] Shinya Takaishi [a]*

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Coordination polymers of iron and 2,5-dihydroxy-1,4- benzoquinone based ligands have been emerging out as a new exciting material because of its appealing features of exhibiting redox activity and possessing high electrical conductivity which also make them potent candidate to be incorporated as a cathode in LIB. The specific capacity of the material is further limited by redox inactivity of iron in case of Fe^{2+}containing MOF ($Fe^{2+} \rightarrow Fe^0$ does not proceed in the cathode reaction).[1] Although Fe redox can be used with Fe^{3+} containing MOFs, it is generally difficult to proceed with the cation insertion reaction in Fe^{3+} MOFs because the pore is occupied by a bulky cation that is difficult to desorb.[2]

In this study, we synthesized a microporous [$Fe_2(dhbq)_3$] MOF containing Fe^{3+} without incorporating extra cations. The MOF is buildup of Fe(III) and $dhbq^{2-}$ ligand which exhibits redox activity based on metal and ligand with a theoretical capacity of 408 mAh /g. Upon incorporating as a cathode, it exhibited a first discharge capacity of 322 mAh /g stem from metal and ligand-based redox activity. As a result of strong d-π conjugation in a three-dimensional network., it showed relatively high electrical conductivity of 1.2×10^{-2} S cm^{-1}.

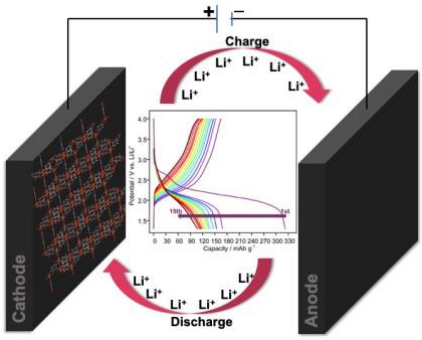

Figure 1. Schematical representation of lithium insertion and desertion.

1) Kon, K., *ACS Appl. Mater. Interfaces* **2021**, *13* (32), 38188–38193. 2) Ziebel, M. E., *J. Am. Chem. Soc.* **2020**, *142* (5), 2653–2664. 3) Murase, R., *Inorg. Chem.* **2017**, *56* (15), 9025–9035. 4) Darago, L. E., *J. Am. Chem. Soc.* **2015**, *137* (50), 15703–15711.