

A comparative study on the application of synthetic 2D MOFs as active materials in hybrid supercapacitors

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Two-dimensional (2D) conjugated metal-organic frameworks (c-MOFs) composed of metal ions and organic ligands have emerged as promising active nanostructured materials for electrochemical energy storage devices.¹ Their unique 2D structure made of regular open channels, large surface area, and abundant redox-active sites of the 2D c-MOFs make them a promising active material for the development of next-generation supercapacitors (SCs).² We designed and produced SC electrodes based on nanoscale hexahydroxybenzene-Cu (HHB-Cu), a representative example of $M_3(C_6X_6)_2$ ($X = N, S, O$) c-MOF family. While c-MOFs with porous structures have been extensively studied in SCs, there is limited research on the electrochemical properties of their counterparts with non-porous structures. The comparison between 2D c-MOFs sharing the same chemistry but different structural properties can provide novel insights into their rational design for electrochemical applications. In this study, we investigate the electrochemical behavior of HHB-Cu with porous and non-porous structures (p-MOF and np-MOF, respectively) in the organic electrolyte (Lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate, 1.0 M $LiPF_6$ in EC/DMC=50/50 (v/v)) in a 3-electrode system by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy. Our CV and GCD data indicated that the p-MOF electrode shows capacities larger than the np-MOF, implying that porosity plays a crucial role in the Li-ion intercalation mechanisms.³ The p-MOF yields a specific capacity of 63 mAh g^{-1} at 0.02 A g^{-1} , a capacity retention of 15% at 10 A g^{-1} , and moderate cyclic stability (66% after 1000 cycles). The specific capacity of the np-MOF was 44.7 mAh g^{-1} at 0.02 A g^{-1} , which was lower than p-MOF, even though the rate capability (capacitance retention of 25% at 10 A g^{-1}) and cyclic stability (75% after 1000 cycles) were higher than p-MOF. To validate np-MOF and p-MOF electrodes in practical applications, hybrid supercapacitors (HSC) were constructed by using np-MOF/p-MOF as the negative electrode materials and activated carbon (AC) as the positive electrode materials. The hybrid devices have shown a specific capacity of 24.1 mAh g^{-1} for AC//p-MOF and 19.5 mAh g^{-1} for AC//np-MOF at a specific current of 0.05 A g^{-1} . Moreover, AC//p-MOF and AC//np-MOF devices demonstrated capacity retention of 55.5 % and 60.6% at 10 A g^{-1} , respectively, which is +40% and +45%, respectively compared to the pristine c-MOF electrodes. After 1000 GCD cycles, AC//np-MOF and AC//p-MOF retained more than 85% and 80%, respectively, of their initial specific capacities. The results of this study can provide insights into the electrochemical behavior of 2D c-MOFs for their use in electrochemical energy storage devices.

References

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