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ABSTRACT

TITLE: Ni/Co Bimetallic Flower-Like Metal-Organic Frameworks with Enhanced Performance for High-Power Energy Storage Applications
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Abstract Body: Metal-Organic Frameworks (MOFs) are compounds consisting of metal ions coordinated to organic ligands to form crystalline porous structures by self-assembly. They have emerged as a class of crystalline materials with high surface area and porosity, tunable pore size and functionalized surface. Due to the metal nodes in the framework, they provide redox centres facilitating faradaic reactions, and due to their crystalline porous structure they provide easier access for electrolyte diffusion. Thus, they own great electrochemical properties, making them ideal for electrode materials for supercapacitors. However, most reported MOFs own an insulating nature which is a major drawback for their electrochemical applications. A common method to solve this restriction is to incorporate another metallic element to enhance the properties of the electrode material.

Nickel materials demonstrate high specific capacitance and exhibit promising electrochemical properties as electrode materials for supercapacitors, but they own low rate capability and cycle life, which is attributed to their poor structural stability during the fast charge-discharge process. With the addition of another metal ion such as Co$^{2+}$ into the structure, more active sites and improved conductivity can be obtained, while stabilizing the Ni species. The partial substitution of the second metal ions in the inorganic nodes will provide synergistic effects for the bimetallic framework. The ratio between the metals can also be adjusted to tune the physiochemical properties of MOFs.

For all these reasons, bimetallic Ni/Co MOFs are promising materials for electrodes in energy storage applications. Currently, Activated Carbon (AC) is used as electrode material for supercapacitors due to its high conductivity, large number of micropores and high surface area. However, the micropore structure of activated carbon limits pore accessibility and ion diffusion, thus reducing the capacitance and energy density. Transition metal oxides are also used as electrode materials for supercapacitors due to their metal centres, which provide faradaic redox reactions, and their low cost. Though, their poor conductivity leads to a low specific capacitance and causes structural destruction of the materials, thus decreasing the stability of the system.

In this study, using terephthalic and trimesic acid as the linkers, binary Ni/Co MOFs (Ni:Co = 4:1, 3:1, 2:1, 1:1) have been synthesized utilizing a solvothermal method. Various parameters that affect the structure and properties of MOFs such as time, temperature, ligands, Ni/Co ratio, and additives have been investigated. The main focus is on the effect of Co ions that substitute the Ni ones in the framework, how they affect the structure’s stability and the electrochemical properties of the bimetallic Ni/Co MOFs.

These materials have been structurally characterised by SEM, EDX, XRD, XPS, FTIR, TGA, BET and TEM. The morphology consists of 2D interlayered nanosheets with smooth surface that assemble to form 3D microflower-like crystalline structures. The addition of Co$^{2+}$ leads to a more dense, hierarchical and spherical morphology. The phase of these materials is also identified by Rietveld analysis and is: Ni$_2$(OH)$_2$(C$_4$H$_4$O$_6$) (CCDC no. 985792). The addition of Co$^{2+}$ does not alter the framework but only provides stability. Moreover, these materials have been electrochemically tested by CV, GCD, EIS and cycling measurements. A large specific capacitance of 1503 F/g at 1A/g has been achieved with 70% retention after 3000 cycles. Finally, asymmetric coin cells using these materials and Activated Carbon (AC) have been developed and tested for their capacitance and cycle life.

In conclusion, Ni/Co MOFs have been synthesized and the effect of Co$^{2+}$ in the framework has been investigated. The incorporation of Co$^{2+}$ provides stability and advanced electrochemical properties, making...
these materials promising candidates as electrode materials for supercapacitors.

Attendance: I will attend in San Francisco and present in person between April 10-14, 2023