Synthesis and characterization of proton conductive MOFs with terminal sulfonic groups

Abstract

Metal-organic frameworks (MOFs) are a class of coordination polymers possessing metallic nodes, connected by organic ligands and having voids. The possibility of rational design of these materials, together with their crystalline nature, make these networks not only potential candidates for a variety of industrial applications, but also scientifically interesting, due to the possibility of a profound understanding of the underlying processes, by correlating their properties with the structure at the atomic level. In particular, these frameworks may be used as proton exchange membranes in fuel cells.

In the present study, a procedure for MOF materials synthesis was developed using ligand precursors with a chlorosulfonyl group, which allows for the introduction of sulfonyl/sulfonate groups into the MOF framework in an uncoordinated to the metal center form. This method enabled the preparation of three materials: JUK-13-SO3H, JUK-13-SO3H-SO2 and JUK-14, differing in the structure dimensionality as well as the types of metallic center and linkers. Impregnation of the network with sulfonate groups allowed for obtaining proton-conducting materials featuring medium or high conductivity. Furthermore, post-synthetic treatment of the JUK-14, involving the encapsulation of imidazole molecules, significantly enhanced proton conductivity under anhydrous conditions, while introducing missing linker defects and removing extra-framework cations allowed for an investigation of the relationship between defect formation, stability, and properties. On the other side, JUK-13-SO3H and JUK-13-SO3H-SO2 materials exhibit a stepwise adsorption of water vapor and CO_2 (195 K) and the occurrence of hysteresis between CO_2 adsorption-desorption curves, as well as selective carbon dioxide from the CO_2/N_2 mixture (298 K). Due to the retention of frameworks crystallinity under various conditions, the structures of different crystalline phases of JUKs-13 were refined, allowing for a detailed structure – property relationship analysis. In general, the characterization of the obtained systems involved techniques such as: single-crystal X-ray diffraction (SC-XRD), powder X-ray diffraction (PXRD), N_2, CO_2, and H_2O vapor adsorption measurements, potentiometric titration, thermogravimetric and elemental analysis, as well as electrochemical impedance spectroscopy (EIS), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR).