**THESIS INFORMATION**

Thesis title: “*Synthesis of novel Zr-based Metal-organic frameworks and application in proton conduction*”

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1. SUMMARY

In this dissertation, the synthesis of two novel stable Zr-based metal-organic frameworks, which are built from the sulfonated linkers, were described. All of MOF members were fully characterized their structures and properties by using analyses of SXRD, PXRD, FTIR, TGA, BET, EA, 1H-NMR, etc.

Furthermore, the development of their application for proton membrane of fuel cell by doping strategy of proton agents as imidazole and histamine within MOFs structure was also researched. As expected, two novel Zr(IV)-based metal-organic framework, termed VNU-17 and VNU-23 was successfully synthesized. Subsequently, detailed structural analysis revealed that VNU-17 and VNU-23 owned the bcu topology with the structure highlighted by densely packed sulfonic acid groups lining 6 Å channels. With this structural feature, anchoring strategy has been carried out to dock the proton transfer agent such as imidazole and histamine into the void space of them to enhance the proton conductivity. Remarkably, the proton conductivity of these materials reached 5.93 × 10-3 S cm-1 (at 70 oC, 85% RH) and 1.79 × 10-2 S cm-1 (at 95 °C, 85% RH) for HIm11⊂VNU-17 and His8.2⊂VNU-23, respectively, without any appreciated loss of performance after a long operated time.

 2. OUTCOMES

For the first time, the two novel Zr-MOFs, namely VNU-17, VNU-23 and hybrid materials have been successfully synthesized via doping proton carriers into MOFs. The use of SCXRD combined with the advanced characteristic methods such as PXRD, FT-IR, TGA, BET, 1H-NMR has revealed that the materials adopted bcu topology and the structure was highlighted by densely packed sulfonic acid groups lining 6 Å channels. They exhibited a high thermal, chemical stability and water resistance and suitable for proton exchange membrane of fuel cells

The use of materials containing histamine within MOFs instead of imidazole affords to increase the operating temperature of the proton exchange membrane from 70 oC (for imidazole) to 95 oC (for histamine). As expected, at 85% RH, His8.2⊂VNU-23 showed a proton conductivity of 1.00 × 10-2 S cm-1 at 70 oC and 1.79 × 10-2 S cm-1 at 95 ° C. These values are better when compared to HIm9⊂VNU-17 (1.53 × 10-4 S cm-1), HIm11⊂VNU-17 (5.93 × 10-3 S cm-1) and the conductivity of other MOFs under 85% RH. Besides, His8.2⊂VNU-23 still retained high proton conductivity at 95 oC and without any change of structure after at least 120 hours of operation. This also supports to minimize CO poison with Pt catalyst at the electrode. Furthermore, the novel hybrid materials with high conductivity and structural stability were created at the practical condition of fuel cells.

3. APPLICATIONS AND OUTLOOKS

These results displayed an interesting new exploration in the design and synthesis of MOFs for enhancing proton conduction of proton exchange membrane fuel cells. Subsequently, the prospective research could be further studied regarding the design and synthesis of the chemical-stable MOFs is an important point for the development of advanced materials.

Using the linkers with sulfonate groups in MOFs synthesis process is one of the original vital intent for effective interaction to proton carriers via acid-base interaction. The conductivity of His8,2⊂VNU-23 reached a high value about 10-2 S cm-1 at 95 oC under 85 % RH which was appropriate with practical conditions in use and retained after a long operated time.

These findings demonstrate the potential for systematically fine-tuning such materials for use as electrolyte materials in proton exchange membrane fuel cells.

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