Covalent-organic framework-based electrolytes fabricated for solid-state Li-ion batteries

Even though much effort has been devoted to the development of covalent-organic framework (COF)-based electrolytes, achieving both Li^+ conductivity and high thermal stability remains a significant challenge. Now, as reported in a recent issue of *Chemistry of Materials*, researchers from Nanjing University of Science and Technology in China have constructed three crystalline thiophene-based imine-linked COFs and explored their Li^+ -conducting properties by doping ionic liquids (ILs) into their one-dimensional (1D) nanochannels. The COF-IL composite electrolytes were found to exhibit excellent thermal stability and high Li^+ conductivities.

Up until this study, confining ILs into the 1D nanochannels of COFs for high-temperature Li^+ conductivity remained an unexplored area. For IL doping, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (IL) was used as a

model ionic liquid and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was used as the lithium salt to investigate Li^+ conduction in the nanochannels of the COFs.

COF-NUST-7 was used as a model host material to accommodate the IL and LiTFSI with different ratios (IL- x @NUST-7 where $x=0.25, 0.5, 0.75$, and 1.0). Successful doping of the IL was possible because of the high porosity and the structure of the 1D nanochannels. A loss of crystallinity was evident for the COFs after doping, indicating that the pores were occupied by the IL. However, the integrity of the chemical structure of the doped COFs was confirmed using a variety of spectroscopic techniques, and it exhibited the same coralline morphology as the pure COF-NUST-7.

After doping, the COFs were explored as lithium solid electrolytes and the results showed their potential to function at higher temperatures (100°C) than polymers, which are the currently used solid electrolytes. Li^+ conductivities of the doped COFs were evaluated in coin cells with a fixed weight ratio of 1:1 (COF-NUST-7

powders/(IL+LiTFSI) and by varying ratios of IL to LiTFSI from 2:1 to 4:1 to 8:1. Results indicate a dependence of ionic conductivity on the IL/LiTFSI ratio, which could be attributed to more expedited ion migration pathways with increasing ratios, where doped mixtures have lower viscosity and higher fluidity.

To investigate the impact of doping amounts on the Li^+ conduction, a fixed ratio of 4:1 IL/LiTFSI was used while the ratios of (IL+LiTFSI)/COF-NUST-7 powder mixtures were modulated

at 25%, 50%, 75%, and 100 percent. It was observed that lowering the doping amounts led to a decrease in ionic conductivity. In addition, the other two COF powders (IL@COF-NUST-8 and IL@COF-NUST-9) were also explored as lithium electrolytes. The selected ratios were IL/LiTFSI at 4:1 and (IL+LiTFSI)/COF powders at 1:1. IL-1.0@NUST-9 possessed the highest ionic conductivity among the materials explored in the study with a value of $2.60 \times 10^{-3} \text{ S/cm}$.

The long-term Li^+ conductivity maintaining tests of IL-1.0@NUST-7 at 120°C for 52 h demonstrated a stable ionic conductivity of $9.10 \times 10^{-4} \text{ S/cm}$, which can be attributed to the thermal stability of the COF structure. Its application was further explored in a solid-state LiFePO_4 -Li full cell system. The full cell demonstrated stable cycling and a high initial discharge specific capacity of 140.8 mA h/g in the first cycle and a Coulombic efficiency of 92 percent. Even after 60 cycles it maintained a discharge capacity of 131.3 mA h/g and a Coulombic efficiency of 99.0 percent.

A Li|electrode|Li cell was also used to investigate the interfacial stability between the COFs electrolyte and the Li metal anode. Results showed that it could be cycled for more than 375 h with an overpotential of only 36.6 mV, which indicates good interfacial stability.

The thiophene-based imine-linked COFs presented in this study can be used as powerful hosts for large amounts of lithium ionic liquids to achieve high Li^+ conductivity within a wide temperature range. This work sets the foundation for the development of COF-based solid electrolytes with high ionic conductivities through doping strategies and shows their potential for use in solid-state lithium-ion batteries.

Xaimara Santiago-Maldonado

Crystalline thiophene-based imine-linked covalent organic frameworks were constructed and explored as Li^+ -conducting composite electrolytes by doping ionic liquids into their 1D nanochannels. Credit: *Chemistry of Materials*.