

Ionic Liquids-loaded Metal-Organic Frameworks System towards the Application for Nanoionic Devices

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Abstract

Metal-Organic Frameworks (MOFs), which is three-dimensional nanoporous materials composed of metal ions and organic ligands coordinated together, has recently attracted enormous attention as functional materials owing to their structural and functional flexibility in the material design for uniformly sized nanopores. In order to endow MOFs with higher ionic conductivity, we loaded ionic liquids (ILs), which are ionic compounds (salts) that show low melting points at around room temperature, into the nanopores of MOFs. As a result, superior characteristics of ILs, such as high ionic conductivity, non-volatility, less flammable nature, and a wide potential window, strongly dominated the physical and electrical properties of MOFs, suggesting that the ILs can be used as “solid electrolytes” towards the application for nanoionic devices without compromising its original property by being loaded into the nanopores of MOFs.

1. Introduction

Although there are several reports so far that investigated the electrical properties of metal-organic frameworks (MOFs) for the use of nanodevices, most of their experiments has been done using pellet or polycrystalline film samples from which it was difficult to extract intrinsic bulk properties due to a lot of grain boundaries [1, 2]. Moreover, ionic liquids (ILs)-loaded MOFs for the application of nanoionic devices, such as memory and neuromorphic device [3, 4], has not yet been discussed so far. In this work, basic investigations in terms of electrical properties for $\text{Cu}_3(\text{btc})_2$ (btc; 1,3,5-benzenetricarboxylic acid) shown in Fig. 1 (a), which are one of the MOFs to be simply synthesized and stable in air, were carried out using single crystalline sample.

2. Experimental

The $\text{Cu}_3(\text{btc})_2$ single crystals were synthesized heating the mixture of the copper (II) nitrate trihydrate (0.45 g), 1,3,5-benzenetricarboxylic acid (0.25 g), N, N-dimethylformamide (10 ml) and 10% nitric acid (20 ml) at 65 °C for 5 days in a screw vial. It was identified that the XRD pattern of the powdered single crystals agrees very well with the simulated one for $\text{Cu}_3(\text{btc})_2$ (not shown). Au electrodes were formed on the crystal surface utilizing Au paste. The area which related to electrical conduction in the single crystal were estimated to be approximately 1 mm thick × 0.3 mm in diameter. For the IL-loaded $\text{Cu}_3(\text{btc})_2$, we prepared [emim][TFSI] (1-Ethyl-3-

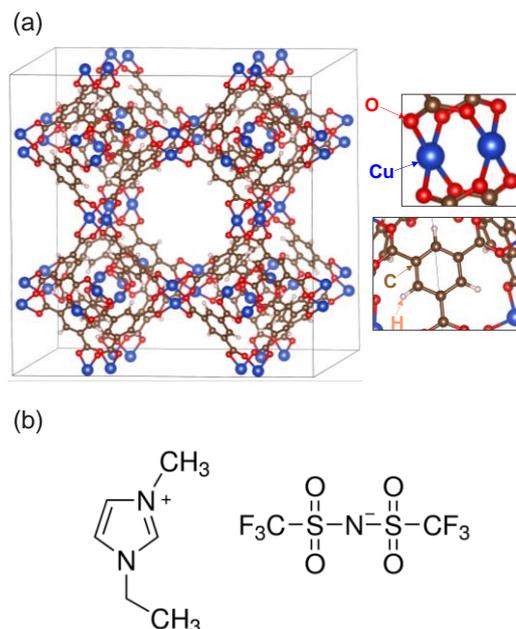


Figure 1. (a) Crystal structure of $\text{Cu}_3(\text{btc})_2$ where blue, red, brown, beige balls indicate Cu, O, C, H atoms, respectively. (b) Structural formula of emim⁺ cation (left) and TFSI⁻ anion (right) in [emim][TFSI].

methylimidazolium bis(trifluoromethylsulfonyl)imide; Fig. 1 (b)) and immersed the single crystals in them. The immersed single crystals were, then, heated in vacuum at 100 °C for 6 hours to make the viscosity of [emim][TFSI] lower and facilitate infiltration into the nanopores of $\text{Cu}_3(\text{btc})_2$. Residual [emim][TFSI] covering the crystal surface was all wiped before electrical measurement. Two terminal electrical measurements were carried out using a source measure unit (Keysight B2901A) for electrical conductivity and electromotive force measurement, and an impedance analyzer (HI-OKI IM3520) for electrochemical impedance spectroscopy.

3. Results and discussion

Figure 2 indicates the DC current-voltage (I - V) characteristics of the Au/ $\text{Cu}_3(\text{btc})_2$ /Au structure measured in air at room temperature and an optical micrograph of the sample structure in the inset. We confirmed that it shows nonlinear behavior where the current abruptly increased around 3 V. In order to examine the electrical conduction mechanism, we investigate the temperature dependence of the DC current between 30 ~ 110 °C, as shown in Fig. 3 (a). It was confirmed that the current at 10 V drastically reduced down to 3×10^{-10}

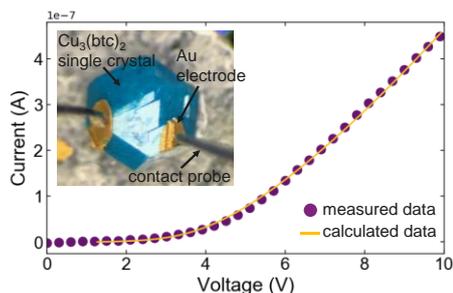


Figure 2. I - V characteristics of $\text{Cu}_3(\text{btc})_2$ single crystal measured in air. Inset shows an optical micrograph of the sample.

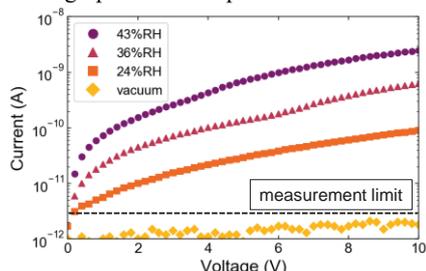


Figure 4. I - V characteristics of $\text{Cu}_3(\text{btc})_2$ single crystal as a function of humidity.

A with increasing temperature whereas the current at 30 °C shows around 1×10^{-6} A. Those in both heating and cooling process almost agreed. Thermogravimetric analysis revealed that the mass loss of the crystals which arises from desorption of the pore-filling water occurs until around 100 °C, as shown in Fig. 3 (b). In Fig. 4, we further evaluated humidity dependence of the I - V characteristics between 24%RH ~ 43%RH to investigate the effect of moisture in air. As expected from the thermogravimetric analysis, the current decreased with decreasing humidity and it was not even detected in vacuum where there is no moisture. Based on these results, it can be considered that the current we measured was attributed to the ionic conduction, in which the proton (H^+) and/or hydroxide ion (OH^-) may be dominant, due to the electrolysis of pore-filling water absorbed by capillary condensation, not to the electronic conduction. The validity of this idea was confirmed by fitting the I - V characteristics with a model for water electrolysis based on Butler-Volmer kinetics, as shown in Fig. 2.

In order to endow $\text{Cu}_3(\text{btc})_2$ with higher ionic conductivity, we filled an [emim][TFSI], which is the highly hydrophobic and stable ionic liquid, into the nanopores of $\text{Cu}_3(\text{btc})_2$. Figure 5 (a) shows a Nyquist diagram between 1~200 kHz obtained on Au/[emim][TFSI]-loaded $\text{Cu}_3(\text{btc})_2$ /Au measured between -30 ~ 23 °C in vacuum and the inset indicates the one obtained on bulk [emim][TFSI] under the same measurement condition. It was indicated that the Au/[emim][TFSI]-loaded $\text{Cu}_3(\text{btc})_2$ /Au showed ionic conduction (6.5×10^{-5} S/cm at 23 °C) even in vacuum, thanks to the non-volatile nature of [emim][TFSI]. On the other hand, IL-unloaded samples showed that there was no detectable ionic conduction (not shown) because of desorption of the pore-filling water in vacuum, as expected from the DC I - V experiments. Here, in order to investigate whether it is possible that the [emim][TFSI] retains its transport property of ions even in the nanopores of $\text{Cu}_3(\text{btc})_2$, the activation energies of

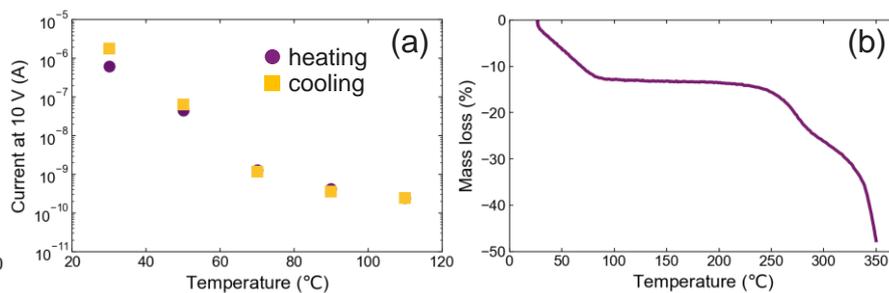


Figure 3. (a) Temperature dependence of the measured DC current at 10V between 30 ~ 110 °C. (b) Mass loss of the $\text{Cu}_3(\text{btc})_2$ single crystal during heating up to 350 °C. Collapse of the crystal structure $\text{Cu}_3(\text{btc})_2$ started at around 250 °C.

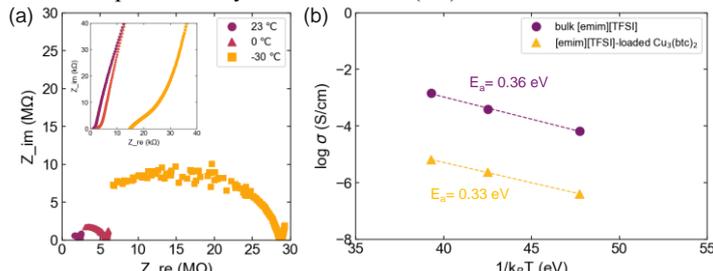


Figure 5. (a) Nyquist diagram obtained on [emim][TFSI]-loaded $\text{Cu}_3(\text{btc})_2$. Inset shows the one of bulk [emim][TFSI] (b) Arrhenius plot of conductivity and extracted E_a for both samples.

the ionic conduction for [emim][TFSI]-loaded $\text{Cu}_3(\text{btc})_2$ and [emim][TFSI] were extracted and compared, as shown in Fig. 5 (b). Both the ionic conductivities decreased with decreasing temperature until -30 °C conforming to Arrhenius law. The extracted activation energies for [emim][TFSI]-loaded $\text{Cu}_3(\text{btc})_2$ (0.33 eV) and bulk [emim][TFSI] (0.36 eV) were almost comparable, indicating that the degree of freedom for ionic motion in [emim][TFSI] was, surprisingly, not limited by being confined into the nanopores of $\text{Cu}_3(\text{btc})_2$.

4. Conclusions

We clarified that the frameworks of $\text{Cu}_3(\text{btc})_2$ itself have very high insulating characteristics and the electrical properties of pore-filling solvent absorbed by capillary condensation strongly dominate the one of $\text{Cu}_3(\text{btc})_2$. The both activation energies extracted from the temperature dependence of ion conductivities for [emim][TFSI]-loaded $\text{Cu}_3(\text{btc})_2$ and bulk [emim][TFSI] were comparable, indicating that the $\text{Cu}_3(\text{btc})_2$ enables to retain the [emim][TFSI] in the nanopores without compromising its original transport property of ions. The “ILs \times MOFs” system provides novel solid electrolytes which have large design space for the next generation nanoionic devices.

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