

Investigation of reaction mechanism of crystalline aromatic dicarboxylate in Li⁺ intercalation by hard X-ray photoelectron spectroscopy

While the demand for lithium-ion batteries (LIBs) is rapidly increasing with widespread electrification of energy systems, LIBs used in practice most often involve electrodes based on inorganic materials, causing ongoing discourse concerning the depletion of raw materials. Such a circumstance motivates researchers to develop sustainable battery technologies effectively using organic electrode materials. However, previous studies on organic electrode materials have focused only on their synthesis or properties. The lack of a systematic understanding of their charge storage mechanism prevents their practical application.

In this study, we systematically analyzed a series of crystalline aromatic dicarboxylate lithium salts, which is a promising group of organic electrode materials also known as intercalated metal-organic frameworks (iMOFs), by shedding light on their electrochemical reaction mechanism [1]. iMOFs, consisting of alternately lavered π-stacked aromatic units and tetrahedral LiO₄ units, show reversible intercalation of two electrons with two Li⁺ ions for charge compensation at the potential of 0.5-1.0 V vs Li/Li⁺, as shown in Fig. 1 [2]. We discovered, through various electrochemical analyses, that the phase transition mechanism of iMOFs during Li⁺ intercalation/deintercalation depends on the aromatic unit. As summarized in Fig. 2, iMOF with a naphthalene framework [2,6-Naph(COOLi)2] strongly interacts with the intercalated Li⁺ ions, resulting in the low Li⁺ diffusivity and the two-phase coexistence at the initial stage of Li⁺ intercalation and deintercalation. In contrast, iMOF with a biphenyl framework [4,4'-Bph(COOLi)₂], with a weak Li⁺ interaction, provides high Li⁺ diffusivity and the solid-solution phase over the entire region. These differences in the phase transition mechanism and Li⁺ diffusivity can give rise to the difference in high-rate capability of charge/ discharge performance [3].

To investigate the reaction mechanism and interactions between the host matrix of iMOFs and intercalated Li⁺ ions in greater detail, hard X-ray photoelectron spectroscopy (HAXPES) experiments were performed at SPring-8 **BL16XU**. Compared with laboratory-scale X-ray photoelectron spectroscopy, HAXPES can provide more information about bonding states or energy states of electrode materials because hard X-rays can access deeper areas within electrodes. Figure 3 shows the obtained C1*s* HAXPES spectra of iMOFs with various amounts of intercalated Li⁺ ions, *x*. In the spectra of both iMOFs, a new peak was observed at 283 eV after Li⁺ intercalation, originating from the bond between aromatic carbon atoms and intercalated Li⁺ ions (C-Li bond). This suggests that intercalated Li⁺ ions are stabilized through their interaction with aromatic carbon atoms (i.e., $Li^+-\pi$ interaction). Interestingly, the C-Li bond peaks of both samples were also observed in the spectra of post-Li+-intercalated samples with x = 0, indicating that intercalated Li⁺ ions are not fully deintercalated. The intensity of the C-Li bond peak relative to the C-C bond peak at 285 eV is higher for the 2,6-Naph(COOLi)₂ sample than for the 4,4'-Bph(COOLi)₂ sample, which suggests that more Li⁺ ions remain in 2,6-Naph(COOLi)₂, probably because of the stronger interaction of the naphthalene framework with Li⁺ ions. This is consistent with the results of electrochemical analyses (Fig. 2). Here, we consider factors governing the Li⁺ $-\pi$ interaction in iMOFs. It is known that the Li⁺ $-\pi$ interaction becomes stronger with decreasing distance between Li⁺ ions and π -electron systems or increasing charge density of π -electrons [4]. Among these factors, the charge density of π -electrons is probably higher for 2,6-Naph(COOLi)2 than for 4,4'-Bph(COOLi)2 because the naphthalene framework exhibits high planarity compared with the biphenyl framework, whose planarity is lowered owing to the rotation



Fig. 1. Li⁺ intercalation and deintercalation in iMOFs with (a) naphthalene framework $[2,6-Naph(COOLi)_2]$ and (b) biphenyl framework $[4,4'-Bph(COOLi)_2]$. Blue, pink, red, yellow, and orange spheres represent C, H, O, pristine Li⁺, and intercalated Li⁺, respectively. 2,6-Naph(COOLi)_2 has two models of the Li⁺-intercalated phases, that is, thermodynamically and kinetically stable phases (respectively, model 1 and model 2), whereas the Li⁺ intercalation into 4,4'-Bph(COOLi)_2 results in the formation of only the "middle" phase [3,5].



Fig. 2. Phase transition mechanism during Li^+ intercalation/deintercalation in iMOFs, and its relationship with the crystal structure.

of its single C–C bond. Consequently, the Li⁺ $-\pi$ interaction can be stronger in 2,6-Naph(COOLi)₂ than in 4,4'-Bph(COOLi)₂.

Furthermore, we discuss the reaction mechanism of iMOFs in terms of the shift of the C–Li bond peak at 283 eV relative to the C–C bond peak at 285 eV in the C1s HAXPES spectra. The peak shift of the C–Li bond, depending on x, can be attributed to differential charging, the effects of the formation of a solid electrolyte interphase (SEI), and/or changes in the chemical states of samples. In our data, differential charging can be ignored because of their symmetric peak shapes. The effects of SEI formation can also



Fig. 3. *Ex situ* C1s HAXPES spectra of (a) 2,6-Naph(COOLi)₂ and (b) 4,4'-Bph(COOLi)₂ samples with various amounts of intercalated Li⁺ ions, *x*. The samples were prepared using coin-type cells composed of iMOF as the working electrode and Li metal as the counter electrode. The cells were charged and discharged at a constant current of C/10, during which charging/discharging was stopped when predetermined amounts of Li⁺ ions were intercalated in the 1st cycle. The resulting cells were disassembled in argon atmosphere, and the iMOF electrodes after washing with dimethyl carbonate were used for HAXPES experiments.

be ignored because the peak shift occurs after SEI formation. Therefore, the peak shift probably originates from the change in the chemical states of samples. In the spectra of 4,4'-Bph(COOLi)₂ samples (Fig. 3(b)), the C-Li peak shifts to a higher binding energy with Li* intercalation. The observed peak shift can be simply attributed to the increase in the Fermi level as a result of the filling of the conduction band by Li⁺ doping. In contrast, the peak shift towards a lower binding energy with Li⁺ intercalation in the 2,6-Naph(COOLi)₂ samples (Fig. 3(a)) implies that reactions that lower the Fermi level can simultaneously proceed with Li⁺ intercalation. From the band structure of 2,6-Naph(COOLi)₂ samples [5], we can propose the relaxation from the kinetically stable Li⁺-intercalated phase (model 2 in Fig. 1(a)) to the thermodynamically stable phase (model 1 in Fig. 1(a)) as a possible reaction. These differences between 2,6-Naph(COOLi)₂ and 4,4'-Bph(COOLi)₂ are partly attributed to the fact that 4,4'-Bph(COOLi)₂ has only one Li⁺-intercalated phase, which can ultimately be related to the strength of the Li⁺ $-\pi$ interaction: the Li⁺ $-\pi$ interaction in biphenyl frameworks is not very strong so the intercalated Li⁺ ions are not tightly trapped between π -stacked layers, unlike in 2,6-Naph(COOLi)₂, resulting in the formation of only the "middle" phase in which intercalated Li⁺ ions can be stabilized by both oxygen atoms of LiO₄ tetrahedra and carbon atoms of biphenyl frameworks.

To conclude, we demonstrated by HAXPES experiments and electrochemical analyses that the electrochemical reaction mechanism and the associated properties in iMOFs are predominantly affected by interactions between the aromatic units and the intercalated Li⁺ ions. The Li⁺ $-\pi$ interaction can be modified by the organic framework, particularly the curvature of the aromatic unit. We thus believe that these findings will be helpful in designing organic electrode materials with the aim of achieving fast-charging performance for their application.

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