

Construction of Solid Electrolytes by using Inorganic-Organic Hybrid Crystals

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1 Introduction

Solid electrolytes are crucial materials for lithium-ion or fuel-cell battery technology due to their structural stability and easiness for handling. Emergence of high conductivity in the solid electrolytes requires precise control of the composition and structure. A promising strategy toward highly conductive solid electrolytes is to employ thermally stable inorganic component and structurally flexible organic moiety to construct inorganic-organic hybrid materials. [1]

We report here syntheses and structures of Li⁺ cation-containing hybrid crystals by using decavacate ([V₁₀O₂₈]⁶⁻, V₁₀) anion and surfactant (*n*-octylammonium, [C₈H₁₇NH₃]⁺, C₈NH₃) cations. [2] Two types of crystals with and without Li⁺ cation, C₈NH₃-V₁₀ and C₈NH₃-Li-V₁₀, were obtained as single crystals.

2 Experiment

The synthetic procedures are simple ion-exchange reactions. C₈NH₃-V₁₀ without Li⁺ cation was synthesized by adding pH-adjusted V₂O₅ aqueous solution (pH 6.0) to C₈NH₃ ethanol solution. Obtained yellow-orange precipitates of C₈NH₃-V₁₀ were filtered off, and washed with ethanol. Yellow rod crystals were obtained from the filtrate or aqueous solution of C₈NH₃-V₁₀. Yellow platelet crystals of C₈NH₃-Li-V₁₀ with Li⁺ cation were obtained from the washing ethanol solution of the precipitates of C₈NH₃-V₁₀. Conductivity measurements were carried out by alternating current (AC) impedance method under a dry Ar atmosphere at 403 or 413 K. X-ray diffraction measurements were performed at the PF-AR NW2A beamline as well as with a laboratory diffractometer.

3 Results and Discussion

The precise control of synthetic procedure enabled the introduction of Li⁺ cation by compositional control. The C₈NH₃-Li-V₁₀ is the first polyoxometalate-surfactant crystal with Li⁺ cation introduced.

The formula of C₈NH₃-V₁₀ without Li⁺ cation was [(C₈H₁₇)NH₃]₆[V₁₀O₂₈]·2H₂O, revealed by the single crystal X-ray analysis. Six C₈NH₃ cations (1+ charge) were associated with one V₁₀ anion (6- charge) due to the charge compensation. No other small counter cation was included, although V₁₀ anion tends to be hybridized with several numbers of proton in the crystals. The crystal packing consisted of alternating V₁₀ inorganic monolayers parallel to the *bc* plane and C₈NH₃ surfactant organic layers with a layered distance of 20.8 Å (Fig. 1a).

C₈NH₃-Li-V₁₀ with Li⁺ cation was formulated to be [(C₈H₁₇)NH₃]₄Li₂[V₁₀O₂₈]·4C₂H₅OH·6H₂O, and four

C₈NH₃ and two Li⁺ cations were associated with one V₁₀ anion (Fig. 1b). The Li⁺ cations exhibited four-coordination geometry, connected to O atoms of water molecules and of V₁₀ anion to form an anion formulated as {[Li(H₂O)₃]₂[V₁₀O₂₈]}⁴⁻ (denoted as Li₂V₁₀). The crystal packing consisted of alternating Li₂V₁₀ inorganic monolayers and C₈NH₃ organic layers (Fig. 1b) with a layered distance of 21.5 Å.

The anhydrous conductivities at the intermediate temperature range were 8.2 × 10⁻⁸ S cm⁻¹ for C₈NH₃-V₁₀, and 1.1 × 10⁻⁸ S cm⁻¹ for C₈NH₃-Li-V₁₀. The lower conductivity of C₈NH₃-Li-V₁₀ may be because the Li⁺ cations were in the O-H···O hydrogen bonding network through the water ligands, which plausibly prevented easy movement of the Li⁺ cations.

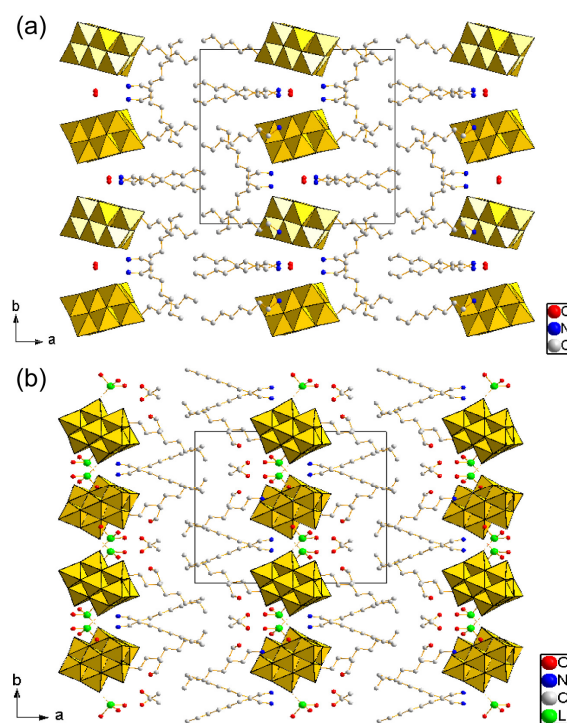


Fig. 1: Crystal structures of (a) C₈NH₃-V₁₀ and (b) C₈NH₃-Li-V₁₀.

References

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