

Synthesis and ionic conduction of a novel lithium salt of gallate anion with high lithium ion conductivity.

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Lithium ion transport number in aprotic organic electrolyte is generally lower than 0.5, because of strong interaction between the lithium ion and aprotic organic molecules. In order to enhance the lithium ion transport number, large anions whose charge is delocalized have been developed^[1]. In the present work, we report on the synthesis and ionic conduction of a novel lithium salt based on a gallium alkoxide anion, lithium tetra(1,1,1,3,3,3-hexafluoro-2-propyl) gallium alkoxide (LiGa(HFIP)₄), in several organic solvents. The large size and charge delocalization of the anion, due to the coordination of four electron-withdrawing groups with central Ga atom, should decrease columbic interaction between the lithium ion and the gallium alkoxide anion and increase the lithium ion transport number.

Required LiGa(HFIP)₄ was prepared from HFIP in two steps as shown in Figure 1.

Figure 2 shows the temperature dependence of ionic conductivity for the organic solvents electrolytes containing LiGa(HFIP)₄. The concentration of the lithium salt is 0.2 mol l⁻¹. The ionic conductivity increases DEC < PC < EC:DEC < DME < THF based solution. Compared with LiPF₆ PC solution, ionic conductivity of 0.2 mol l⁻¹ LiGa(HFIP)₄ PC solution is lower. However, the higher degrees of dissociation and lower anionic mobility of LiGa(HFIP)₄ are expected than those of LiPF₆ because the anionic size of Ga(HFIP)₄⁻ is larger than that of PF₆⁻.

In order to clarify local structure of the anion in the aprotic solvents, we combine the results of Ga *K*-edge EXAFS with first principle molecular orbital calculations. Figure 3 shows the correlation between the lengths of Ga-O and solvation energies of lithium ion in the solvents. The length between the central gallium and oxygen was obtained by Ga *K*-edge EXAFS. The solvation energy was calculated by *Ab initio* Hartree-Fock self-consistent field molecular orbital calculations and density functional theory calculations which was carried out by Gaussian03 program. The geometry for lithium ion coordinating with four solvent molecules was optimized at HF/3-21G. Then single point energy was calculated for the optimized structure at B3LYP/6-311+G(d,p). The same procedure was carried out for LiGa(HFIP)₄ and Ga(HFIP)₄⁻. The comparison for the optimized structure of LiGa(HFIP)₄ with Ga(HFIP)₄⁻ suggested that the average length of four Ga-O bonds of LiGa(HFIP)₄ is shorter than that of Ga(HFIP)₄⁻. Accordingly, the interaction between the lithium ion and the anion should become stronger with decreasing the average length of four Ga-O bonds of LiGa(HFIP)₄. It is also suggested that the interaction between lithium ion and solvent is strong when the solvation energy is large in absolute value. That is, the larger solvation energy is, the weaker interaction between lithium ion and anion become. The tendency of the correlation in Figure 3 agrees with the suggestions about the interaction. Consequently, the length of Ga-O

obtained by Ga *K*-edge EXAFS relates the calculated solvation energy of lithium ion.

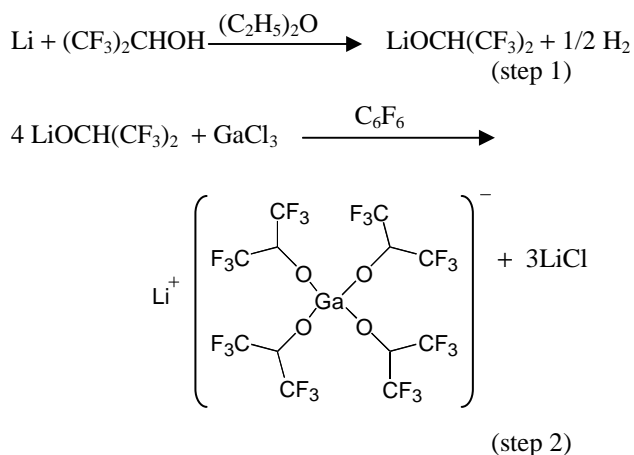


Fig.1
Reaction scheme for preparation of LiGa(HFIP)₄.

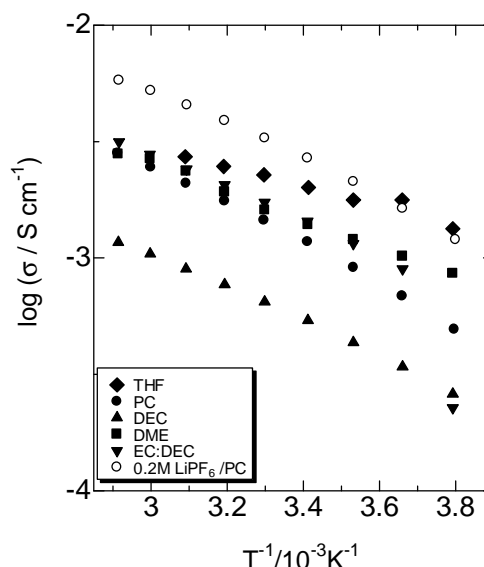


Fig.2
Temperature dependence of ionic conductivity of 0.2 mol l⁻¹ LiGa(HFIP)₄/solvents. ◆:tetrahydrofuran, ●:propylene carbonate, ▲:diethyl carbonate, ■:1,2-dimethoxyethane, ▼:ethylene carbonate: diethyl carbonate=1:1 mixture, ○: 0.2 mol l⁻¹ lithium hexafluorophosphate propylene carbonate.

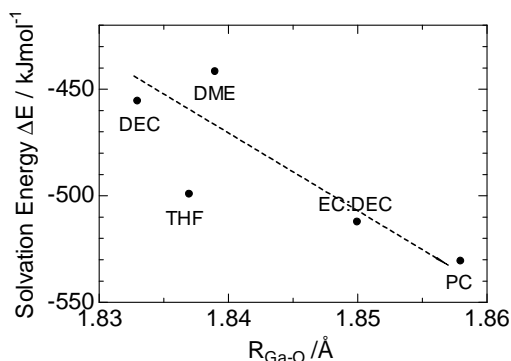


Fig.3
Correlation between solvation energy and the length of Ga-O.

Reference

[1] H.Tokuda and M.Watanabe, *Electrochim.Acta*, **48**, 2085 (2003)