

## Anion Complexation by Calix[4]pyrrole in Solid Polymer Electrolytes

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### Introduction

Solvent-free solid polymer electrolytes have been the issue of intensive study because of their potential use as the electrolyte in electronic devices, such as rechargeable lithium batteries, fuel cells and organic solar cells.<sup>1-4</sup> Ionically conductive polymer electrolytes are formed when a metal salt, MX, is dissolved in a neutral polymer solvent having electron donor atoms such as O or N, where M is normally an alkali metal such as lithium ion and X a fairly soft anion (e.g., I<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, or BF<sub>4</sub><sup>-</sup>). The best-known polymer electrolyte is the complex of lithium salts with poly(ethylene oxide) (PEO), in which the lone pair electrons on the O atoms in PEO complex with Li<sup>+</sup>.<sup>5</sup> The dissolution of a salt into a polymer solvent occurs when the free energy gain upon solvation is sufficiently favorable that it overcomes the lattice energy of the salt. Therefore, the interaction between the metal salt and the solvent determines the extent of dissolution of the metal salt and consequently the concentration of free ions, which are responsible for the ionic conductivity. The ionic conductivity varies with the concentration and the mobility of the charge carriers. Various approaches have been used to increase the ionic conductivity by providing the coordinative interaction between the metal cation and polymeric ligand (i.e., cation complexation).<sup>6,7</sup> Although the structures of polymer electrolytes vary, the source of the

ionic conductivity is the same in all systems; the interaction between cation and ligand is very important in determining the ionic conductivity.

An alternative approach to increasing the ionic conductivity is to exploit the interaction between the anion of the metal salt and the solvent (i.e., anion complexation). Under this approach, the metal ions become relatively free and more mobile, whereas the movement of anions is restricted. Thus, anion complexation should give much better performance than cation complexation in applications such as lithium battery electrolytes. McBreen *et al.*,<sup>8-11</sup> approached the similar idea in solution, resulted in the increase in conductivity of lithium battery electrolytes.

A tremendous amount of effort has been devoted to the design and synthesis of receptor molecules for selective complexation of anions, predominantly in the biological sciences, where the emphasis has been on molecular recognition and mimicking biological processes. Most anion-complexing compounds are unsuitable for use in a neutral polymer matrix because they have either positively charged binding sites;<sup>12</sup> hence in the present study we used the neutral entity calix[4]pyrrole (CP) as the anion-complexing compound. Calix[4]pyrrole showed a marked preference for F<sup>-</sup> and Cl<sup>-</sup> relative to other anion guests (Br<sup>-</sup> or I<sup>-</sup>) in solution of their tetrabutylammonium salt.<sup>13</sup>

### Experimental

We prepared poly(vinyl chloride) (PVC, M<sub>w</sub>=200,000, Aldrich Chem. Co.) derived electrolytes containing CP as anion-selective acceptors of lithium salt (LiF, LiCl and LiClO<sub>4</sub>, Aldrich Chem. Co.) to provide mechanical strength in addition to high ionic conductivity. Meso-octamethyl calix[4]pyrrole was synthesized<sup>13-15</sup> and confirmed by NMR. PVC, LiCl (or LiClO<sub>4</sub>) and CP were dissolved in THF. The solution was poured into glass Petri dishes and the THF was evaporated off at room temperature, yielding solid films that were further dried under high vacuum for several days. All try to prepare for a homogeneous film of CP/LiF/PVC system was not succeed because of the unstability of all three components inside of (co)solvents or in dried state. The conductivity of the final polymer electrolyte, at least three samples, was measured at 25 °C and different humidity conditions. The conductivity at the lowest humidity was measured in glove box under Ar after vacuum for 1 day.

In order to determine the gas-phase optimized complex structures, we carried out a theoretical study using density functional theory at the B3LYP level with 6-31G\* and 6-31+G\* basis sets for a CP and a lithium salt, LiX, respectively. To obtain the solvent energy in polymeric medium, the isodensity polarized continuum solvation (IPCM) method<sup>16</sup>

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with isodensity level of 0.001 a.u. was used. The gas-phase optimized geometries were used in the IPCM calculation.

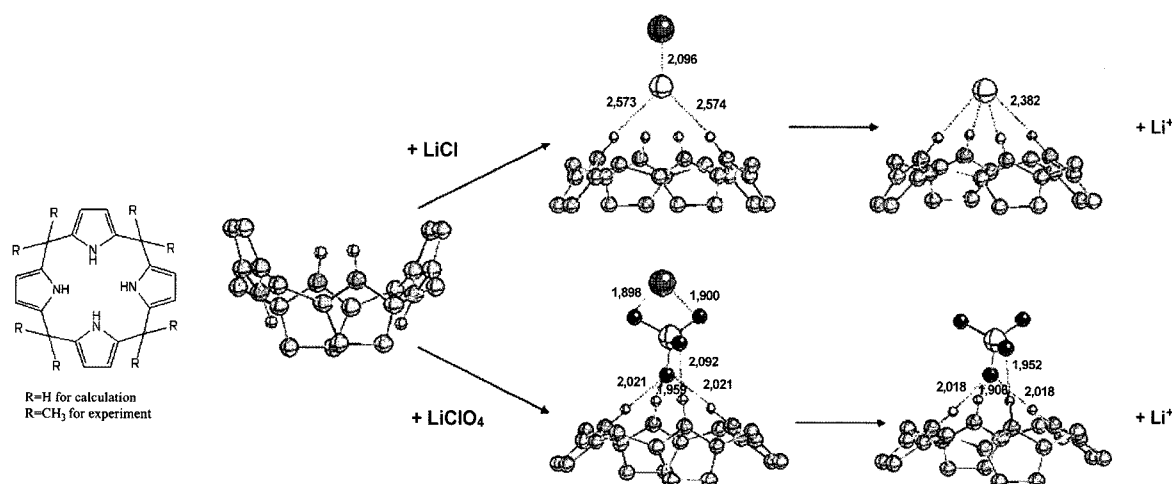
## Results and Discussion

The calculated dissociation energies ( $\Delta G_D$ ) of LiX to Li<sup>+</sup> and X<sup>-</sup> in the gas phase are +145.6 and +131.9 kcal mol<sup>-1</sup> for X=Cl and ClO<sub>4</sub>, respectively. This indicates that the dissociation of LiClO<sub>4</sub> is more favorable than that of LiCl, and hence that if these salts could be dissolved in an appropriate polymer matrix, the conductivity of electrolytes in the polymer matrix with LiClO<sub>4</sub> would be higher than that of the polymer matrix with LiCl. However, when CP is added to LiX to form the CP/LiX complex, the  $\Delta G_D$  value for the CP/LiX complex is +110.8 for CP/LiCl and +111.9 kcal mol<sup>-1</sup> for CP/LiClO<sub>4</sub>, indicating that dissolution of CP/LiCl is more favorable by 1.1 kcal mol<sup>-1</sup> at the gas-phase. The lower dissociation energy of CP/LiCl is due to the much larger stabilizing effect of complexing CP with Cl<sup>-</sup> compared to ClO<sub>4</sub><sup>-</sup>. Moreover, in the presence of the PVC polymer matrix (CP/LiX/PVC) with a dielectric constant of 2.95, the  $\Delta G_D$  values calculated using the IPCM, IPCM-B3LYP//B3LYP, are -18.1 for X=Cl but +25.1 kcal mol<sup>-1</sup> for X=ClO<sub>4</sub> at the gas-phase optimized geometries. This indicates that, due to the solvation effect of PVC, the lithium ion dissociation is much more feasible for the CP/LiCl/PVC complex than for the CP/LiClO<sub>4</sub>/PVC complex and, as a consequence, that the ion conductivity in the CP/LiX/PVC complex is much higher for X=Cl than for X=ClO<sub>4</sub>.

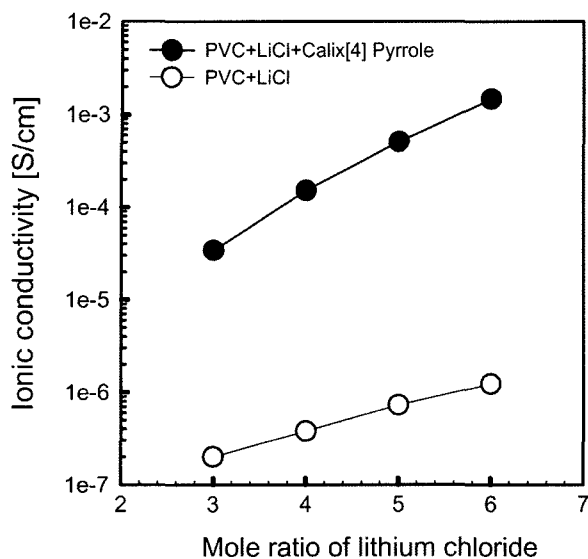
The gas-phase optimized structures of the complexes of CP and LiX are depicted in Figure 1. The CP...X...Li<sup>+</sup> structure depends on the anion type; specifically, the Cl<sup>-</sup> anion is symmetrically bound to four acidic hydrogens of CP, whereas two of the oxygens of ClO<sub>4</sub><sup>-</sup> are effectively bound to four hydrogens.

bound more strongly to Cl<sup>-</sup> than to ClO<sub>4</sub><sup>-</sup>, and as a result, the binding energy of X<sup>-</sup>-Li<sup>+</sup> is reduced more for Cl<sup>-</sup>-Li<sup>+</sup> than for ClO<sub>4</sub><sup>-</sup>-Li<sup>+</sup>, causing the Li<sup>+</sup> cation to become free and more mobile in the CP/LiCl system. This picture is supported by the negative  $\Delta G_D$  value for the CP/LiCl/PVC complex, which implies that the favored equilibrium state is the dissociated state. Therefore, the conductivity of the polymer electrolyte of the CP/LiCl/PVC complex is expected to be higher.

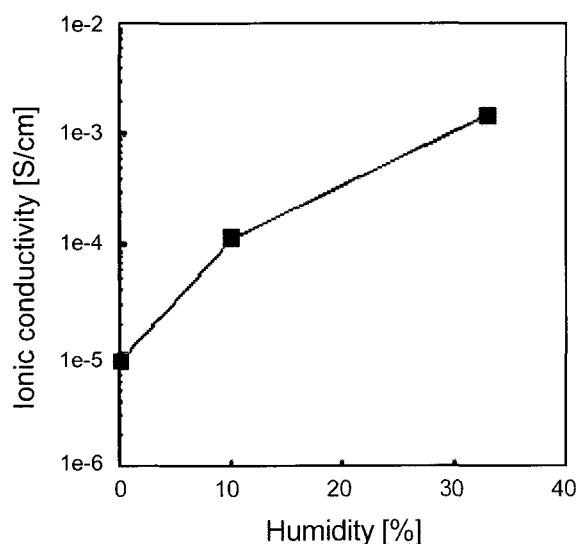
We measured the ionic conductivities of the CP/LiCl/PVC system at various mole fractions of LiCl with the concentration of CP in the PVC matrix fixed at 10 wt% (the maximum concentration that could be used due to miscibility limitations). Figure 2 shows the results of these measurements at a relative humidity of 33%, along with the ionic conductivities of the LiCl/PVC system without CP. Measurements on PVC alone and PVC/CP systems showed their conductivity to be below the detection limit of our instrument ( $\sim 10^{-9}$  S cm<sup>-1</sup>); it is thus considered to be ionically non-conductive. As shown in Figure 2, the ionic conductivity increases with increasing mole ratio of LiX in both the CP/LiCl/PVC and LiCl/PVC systems. Surprisingly, the ion conductivity increased by more than two orders of magnitude when CP was added to the LiCl/PVC matrix. One explanation for this conductivity enhancement is that strong interactions between the PVC-supported CP and the Cl<sup>-</sup> ions lead to the formation of effectively free Li<sup>+</sup> ions for ionic conductivity. The highest ionic conductivity achieved is higher than  $1.5 \times 10^{-3}$  S cm<sup>-1</sup>, which is almost three orders of magnitude higher than that of 0.2 M LiCl in THF ( $1.6 \times 10^{-6}$  S cm<sup>-1</sup>).<sup>17</sup> The ionic conductivity is expected to also depend on the humidity, because water also facilitates the formation of free ions. As expected, the ionic conductivity decreased markedly with decreasing humidity, as shown in Figure 3. The mobility of the polymer chains in the matrix is also



**Figure 1.** Optimized structures of CP and possible complexes between CP and lithium salts (H atoms bonded to carbons are omitted).



**Figure 2.** Ion conductivity dependence of the concentration of LiCl in CP/LiCl/PVC films.



**Figure 3.** Ion conductivity dependence of the relative humidity of PVC-supported CP-LiCl complexed films (it is assumed that the humidity is zero at Ar environment).

known to affect the conductivity. One way to see the chain mobility of PVC is the glass transition temperature, which increased from 93 to 96°C upon addition of the CP/LiCl complex. This increase in glass transition temperature indicates that addition of the CP/LiCl complex lowers the PVC chain mobility, which is expected to reduce the ionic conductivity. However, despite this effect, the ionic conductivity still increased significantly on addition of the CP/LiCl complex, indicating that the effects of anion complexation far outweigh the effects of lower PVC chain mobility.

In contrast to the excellent conductivity of the CP/LiCl/PVC film, the ionic conductivity of the CP/LiClO<sub>4</sub>/PVC film was less than the lower detection limit of our instrument (10<sup>-9</sup> S cm<sup>-1</sup>), and hence this system is considered ionically non-conductive. This result is consistent with our predictions based on the calculation.

## Conclusions

In this paper, we describe a prospective approach to increasing the metal ionic conductivity of solid polymer electrolytes by using the anion complexation between the anion of the metal salt and the solvent matrix. We have prepared a new type of solid polymer electrolyte (CP/LiCl/PVC) and demonstrated its excellent ionic conductivity. The high ionic conductivity of this material is attributed to anion complexation between the anions and their receptors (CPs) dissolved in the PVC matrix. The anion complexation of CP, which should help to increase both the concentration of free Li<sup>+</sup> and its mobility, is more favorable with Cl<sup>-</sup> than ClO<sub>4</sub><sup>-</sup>. Consequently, such systems have high cation conductivity and characteristics of high performance electrolytes that are required to achieve high power density and good rechargeability for lithium batteries.

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