

Polymer-in-salt like conduction behavior of small-molecule electrolytes

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Abnormal salt content dependence of conductivity is observed in solid electrolytes exclusively composed of small molecules of 3-hydroxypropionitrile (HPN) and lithium iodide (LiI) induced by reinforced hydrogen bonding and formation of ionic clusters at high salt content.

It is well known that the conductivity of most liquid and solid electrolytes decreases gradually with increasing salt concentration beyond *ca.* 1 mol l^{-1} due to significant ion association. However, "polymer-in-salt" conduction behavior was observed in polymer-based electrolytes by Angell *et al.*¹ They found that the ionic conductivity of the electrolytes turns to increase with increasing salt concentration beyond a critical point. Thereafter, polymer-in-salt conduction behaviors have been reported in other polymer electrolytes.^{2–5} To our knowledge, all such conduction behaviors are observed only in polymer electrolytes and the proposed conduction mechanisms are also based on the movement of the polymer segments. It seems that the presence of polymer in the electrolyte is essential for the saltation of the conduction behavior at high salt content. Herein, we report a polymer-in-salt conduction behavior in a solid electrolyte only composed of small molecules.

LiI-HPN solid electrolytes were prepared and analyzed in dry argon ($\text{H}_2\text{O} < 1 \text{ ppm}$).[†] Fig. 1 illustrates the dependence of the conductivity on the LiI content in the electrolyte at 30°C . The conductivity decreases drastically as the LiI/HPN molar ratio increases from 1:4 to 1:2, consistent with the behavior of most other electrolytes. As the lowest salt concentration in this work is still rather high with respect to the normally used electrolytes, the conductivity maximum points at low salt concentration is not observed here. However, the conductivity turns to increase beyond 1:2 and reaches its maximum at 2:1. Phase diagram study indicates that no new phases appear within this range of salt concentration. That is, the electrolyte remains a composite between LiI/HPN = 1:2 and 3:1. Clearly, the above salt concentration dependence of the conductivity is abnormal for most other electrolytes but quite similar to the behavior of the polymer-in-salt electrolytes (composite).

In order to find out if HPN and/or LiI have/has been polymerized during sample preparation, mass spectroscopy (MS) is employed to determine the molecular weights of the electrolyte

and its fractures at various LiI/HPN molar ratios (Fig. 2). Although the range of the recorded *amu* values has been extended to 800, only some small molecules can be detected in the electrolyte such as $\text{CH}_2\text{CH}_2\text{CN-Li-OCH}_2\text{CH}_2\text{CN}$ and Li(HPN)_2 . Other peaks can be simply attributed to hydrogen-bonded methanol, $(\text{MeOH})_m$, or the associates of methanol with the above species because methanol was used as the thinner or solvent to the solid electrolyte for the MS analysis. It must be pointed out that the solvent methanol cannot break strong chemical bonds of polymeric molecules though it may break the weak hydrogen bonding and dissolve the ionic species associated to HPN in the electrolyte. This implies that abnormal polymer-in-salt conduction behavior can also occur in electrolytes exclusively composed of small molecules.

The solid electrolytes are then characterized with FTIR and Raman spectroscopy so as to find out the reason for the above abnormal conduction behavior. The disappearance of the strong 3417 cm^{-1} and the appearance of the 3217 cm^{-1} represent, respectively, the breakage of the hydrogen bonding in pure HPN and the formation of $\text{Li}^+\cdots\text{OH}$ associates in the electrolyte (Fig. 3a).⁶ This corresponds to the salt concentration range for normal conduction behavior. However, a broader peak appears at 3489 cm^{-1} as more LiI is added. This band is attributed to the hydrogen bonding between I^- and HO of HPN.⁷ Its intensity surpasses that of the 3217 cm^{-1} band at LiI/HPN = 2:1, indicating that the content of the $\text{I}^-\cdots\text{HO}$ hydrogen bonding in the electrolyte is reinforced while that for the $\text{Li}^+\cdots\text{OH}$ interaction is reduced.

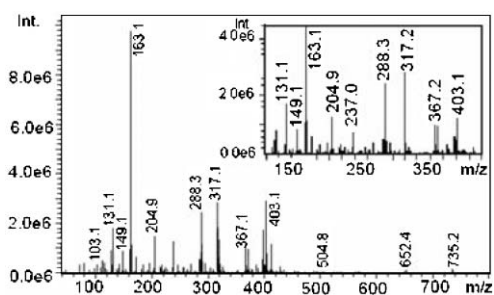


Fig. 2 Typical mass spectrum of the solid electrolyte (at LiI/HPN = 1:1).

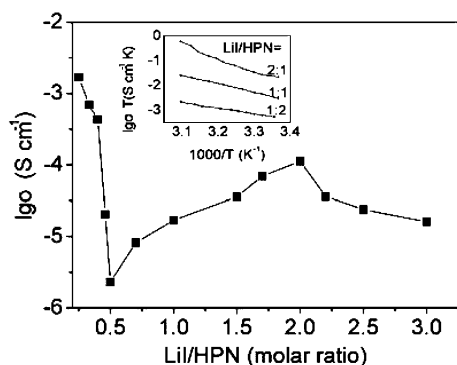


Fig. 1 The salt content dependence of conductivity of LiI/HPN electrolyte at 30°C (inset: Arrhenius plots of conductivity of the composites at different molar ratios of LiI/HPN).

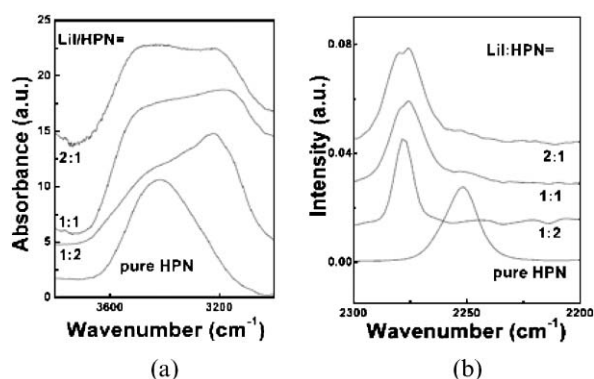


Fig. 3 FTIR spectra of the OH stretching (a) and the Raman spectra of the nitrile stretching (b) of HPN at different LiI/HPN molar ratios.

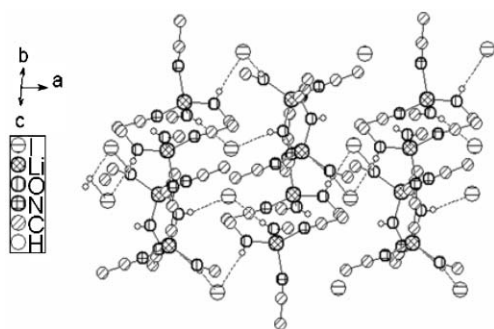


Fig. 4 Part of the H-bonded chain in the structure of $\text{LiI}(\text{HPN})_2$.

The presence of the $\text{I}^- \cdots \text{HO}$ hydrogen bonding insures that a continuous network is constructed and the small molecule-based solid electrolyte acts like a polymer electrolyte.

The electrolyte at $\text{LiI}/\text{HPN} = 1:2$ (molar ratio) has been proved to be one compound before.⁸ Single crystal XRD analysis shows that two hydrogen atoms connect with one iodide atom and form a polymer-like continuous network in this compound (Fig. 4). These results confirm the existence of $\text{I}^- \cdots \text{HO}$ hydrogen bonding and demonstrate clearly that this solid electrolyte is only composed of small molecules.

Raman spectroscopic study indicates that the nitrile stretching band of pure HPN at 2253 cm^{-1} is replaced with a sharp band at 2277 cm^{-1} due to association of Li^+ with the nitrile at $\text{LiI}/\text{HPN} = 1:2$ (Fig. 3b).^{8,9} However, the 2277 cm^{-1} band becomes broad and a new component, at 2280 cm^{-1} , is further split from it with the increase of salt content. The relative intensity of the 2280 cm^{-1} band grows with increasing salt content, similar to our previous spectroscopic observations on the polymer-in-salt conduction behavior of polyacrylonitrile based electrolytes.⁵ Therefore, the presence of the 2280 cm^{-1} band is analogously attributed to the formation of new associates like $[\text{Li}^+_m \text{I}^-_n] \cdots \text{NC}$ ($m > n$) in LiI/HPN electrolyte. In addition, there are also free $[\text{Li}^+_k \text{I}^-_j]$ ($k \neq j$) ionic groups or clusters that are not associated with the polymer-like network. These ionic clusters contribute the most to the polymer-in-salt like conduction behavior in different ways depending on the concentration of the salt in the composite. The ionic clusters connect with each other to form segments of percolation pathways and exchange charges with the ionic species associated with HPN when the salt content is not very high. In this case, the segments of the polymer-like network and the associated ionic species on it act as a transient bridge for the charge exchange and the polymer-in-salt conduction behavior begins to

appear. When the salt content is very high, these individual cluster-composed segments connect and form infinite percolation pathways. They are the most important pathways of ion transport of the electrolyte. The presence of ionic clusters is detrimental to the ion transport in normal electrolyte. However, they contribute the most to the polymer-in-salt like behavior of electrolytes with extremely high salt content because the content of the dissociated ions is very low in this case.

In summary, abnormal conduction behavior has been observed in solid electrolyte composed exclusively of small molecules. This behavior is attributed to the reinforced $\text{I}^- \cdots \text{HO}$ hydrogen bonding and the formation of ionic clusters, $[\text{Li}^+_k \text{I}^-_j]$ ($k \neq j$) and their association with the HPN molecules at high salt content. The former connects the small HPN molecules and insures that the small HPN molecules act as large polymer molecules in the whole while the latter provides finite or infinite percolation pathways. Therefore, an efficient percolation pathway is built up for ion transport at high salt concentrations.

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Notes and references

† The conductivity of the electrolyte was determined with an HP 4192A AC impedance analyzer from 5 Hz to 13 MHz. The vibrational spectra of the electrolytes were recorded on a BIO-RAD FTS-60V FTIR spectrometer and a Bruker RFS 100 FT Raman spectrometer, respectively. The mass spectra (ESI-MS) was measured on an LC MS-2010 spectrometer. The X-ray diffraction (XRD) data for the single crystal were collected on a Rigaku Raxis Rapid IP X-ray diffractometer.

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