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Electrical and electrochemical properties of triphenylene based lithium solvated electron solutions

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Abstract

Conductivity and open circuit potentials of lithium solvated electron solutions (Li SESs) based on triphenylene (TRI) in tetrahydrofuran (THF) were studied. It was found that those solutions with Li:TRI ratio > 0.5 demonstrate much higher conductivity comparing to naphthalene based Li SES of same concentration, which can be related to TRI π -stacking properties. Based on the values of open circuit voltage in a half-cell, the values of entropy and enthalpy change were calculated for the Li:TRI ratios of 2:1 and 4:1. The value of ΔS for $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ is higher than the one for naphthalene based Li SES with Li:PAH ratio = 1:1. The obtained values are much higher of those for solid state electrodes used in lithium ion batteries. Based on quantum chemical modeling of lithium-triphenylene interactions, it was shown that the unusually high values of conductivity could be related to the formation of a dimeric conductive complex.

Introduction

A reaction between lithium metal and solutions of polyaromatic hydrocarbons (PAHs), such as naphthalene and biphenyl, leads to formation of solvated electron solutions (SESs). Previously we reported electrical, electrochemical and physical chemical properties of these solutions for various Li : PAH : THF ratios ^{1,2}. The conductivity of SES demonstrates metal-like behavior due to the electron density delocalization in the PAH anions. Li SES have potential application as liquid based electrodes in novel secondary batteries.^{3,4} In these batteries, it is desirable to obtain a high Li:PAH ratio due to increase of the energy storage capacity. For the application in such batteries, it is desirable to obtain a high Li:PAH ratio together with a low potential versus lithium so as to increase the energy storage capacity of the battery. The conductivity of the Li SESs based on

biphenyl and naphthalene for some concentrations reaches a maximum of ~ 11 mS/cm with the Li:PAH ratio of 2:1 corresponding to two electrons being donated to the aromatic system. Since a larger number of aromatic rings in PAH should increase the number of possible atoms of lithium per PAH molecule in Li SES, recently we studied the formation of these solutions based on corannulene and 1,3,5-triphenylbenzene ⁵ Here we report our investigations on triphenylene, a molecule that can be considered to be naphthalene with two additional fused benzene rings (**Figure 1**).

Experimental

Reagents were purchased from Sigma-Aldrich and used as received. LiSES samples were prepared inside an argon-filled glovebox using anhydrous THF as a solvent.

Since solubility of TRI in THF is lower than for naphthalene and biphenyl, 0.1M solutions (not taking into account the volume expansion upon the PAH dissolution) were the starting point for the studies with the general formula of Li SESs as $\text{Li}_x(\text{TRI})(\text{THF})_{123}$.

Conductivity (σ) vs. temperature (T) measurements

Conductivity (σ) vs. temperature (T) measurements of Li SES were carried out using a modified procedure previously described for the naphthalene-based Li SES [1](#). TetraCon 325 Standard conductivity cell probe that utilizes the four-electrode measuring principle with the measurement range of 1 $\mu\text{S}/\text{m}$ to 2 S/cm was used to measure the conductivity of the Li SES. The probe was attached to a Cond 3310 meter and calibrated using 0.01M KCl solution. A sealed tube containing Li-SES with the probe dipped into the solution was assembled in a glove box. The conductivity vs. temperature measurements were performed out of the glove box using ice-water bath for

cooling down the sealed tube. The conductivity measurements were recorded upon heating up the tube upon removal from an ice bath and the exposure to ambient temperature.

Open-circuit potentials (E) vs temperature (T) measurements of Compound 1-based Li SES

The open-circuit potentials (E) vs temperature (T) profiles were obtained using a Li/Ceramics electrolyte (Ohara, Japan)/Li SES half-cell configuration. The method for measuring E vs T is described in our previous work ^{3,4}. It enables entropy and enthalpy changes to be determined for the half cell

Modelling

Density functional theory (DFT) based calculations with the range-separated functional based on the M06 ⁶ which includes the van der Waals force have been performed with the 6-31g (d,p) basis set to optimize the geometries of the adducts and calculate the binding energies of various structures between lithium atoms and anthracene molecules. The molecular orbitals of the most energetically favored structure were obtained.

Results and Discussion

Conductivity.

The conductivity vs. temperature correlation for $\text{Li}_x(\text{TRI})(\text{THF})_{123}$ solutions ($x = 0.5; 1.0; 2.0; 3.0; 4.0$) and naphthalene based $\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$ is shown in **Figure 2**. Although the conductivity of $\text{Li}_{1.0}(\text{TRI})(\text{THF})_{123}$ is lower than the one for $\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$, the conductivities of all the other solutions are significantly higher. The highest value of conductivity is observed for $\text{Li}_{2.0}(\text{TRI})(\text{THF})_{123}$. This value at 295 K (22 °C) is 17 times higher than for $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{123}$ (**Table 2**). The conductivity of triphenylene based Li SES starts

decreasing upon further increase of Li:TRI ratio, however, the conductivity of $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ at 295 K is still 9.7 times higher than for $\text{Li}_{1.0}(\text{Naphthalene})(\text{THF})_{123}$. This significant difference in conductivity between N and TRI based Li SES may be related to more interactions between triphenylene-Li ion pairs due to triphenylene π -stacking properties. All the $\sigma(T)$ profiles demonstrate quasi-linear correlation, which is similar to metals, as well as to ammonia and PAH based Li SES.

Among the studied Li SES based on triphenylene, the conductivity first increases upon the increase of Li:TRI ratio reaching the peak at 2:1, then decreases (**Figure 3**). This pattern is very similar to diluted naphthalene and biphenyl based solutions with the formula of $\text{Li}_x(\text{PAH})(\text{THF})_{25}$ ^{1,2}.

Thermodynamics data

Based on the conductivity results, the two solutions with the highest conductivity and the highest Li:PAH ratio were chosen for open-circuit potentials (E) vs temperature (T) study. The E vs. T profiles of $\text{Li}_{2.0}(\text{TRI})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ in Li/Ceramics/Li SES half-cell configurations are shown in **Figure 4**. The enthalpy changes (Table 2) and the entropy changes of the half-cell were calculated using the following equations ($n = 1$ for lithium, $F = \text{Faraday constant}$):⁷

$$\Delta S = nF \frac{\partial E}{\partial T}$$

$$\Delta H = -nF \left(E - T \frac{\partial E}{\partial T} \right)$$

Table 3 compares the entropy changes of the half-cell reactions of TRI-based Li SES and those Li SES prepared using naphthalene and biphenyl, against the solid oxide-based LIB cathode material LiCoO_2 ⁸ and the anode material Li_xC_6 ⁹. As can be seen the changes in entropy (ΔS) are much greater for the Li SES than for the standard electrode materials used in LIBs, which can be

attributed to their being in a liquid as opposed to a solid state, which allows for more degrees of freedom. In contrast to Li_xC_6 , where the intercalation process occurs between two solid materials (lithium metal and graphite) giving a solid (Li_xC_6), the formation of Li SES is a process where solid Li metal transfers into a liquid phase, meaning the whole system becomes much more disordered, so entropy values are negative for all $\text{Li}_x(\text{TRI})(\text{THF})_{123}$, as seen from the linear fit equation. Considering relatively low concentration of the studied solutions (123 molecules of THF per molecule of PAH, which is ~ 0.1 M solution of PAH in THF), the interactions between the molecules are much lower than in the solid Li_xC_6 , which prevents phase transition effects, thus, no drastic decrease or increase of ΔS is observed in particular parts of the graph. Also, since the increase of x in $\text{Li}_x(\text{TRI})(\text{THF})_{123}$ does not lead to a change in molecules position against each other in the solution, as happens in the solid (crystal structure changes, changes in interactions between graphite layers, Li – Li interactions, etc.), the linear correlation between the composition and the entropy looks feasible for $\text{Li}_x(\text{TRI})(\text{THF})_{123}$. The ΔS for the triphenylene based Li SES are lower than the values for biphenyl, however, the entropy change value for $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ is higher than the one for $\text{Li}_{1.0}\text{N}(\text{THF})_{24.7}$.

Modeling of intermolecular interactions in triphenylene based Li SES

To better understand the properties of triphenylene based Li SES and interactions between lithium and the PAH, we have modeled structures of triphenylene – lithium adducts with Li:TRI ratios of 2:1 and 4:1. Since the possible reason of unusually high conductivity of TRI based Li SES comparing to naphthalene is conductive complex formation due to Li-triphenylene-stacking, we have also performed modeling of corresponding dimeric structures with the formula $\text{Li}_{2x}(\text{TRI})_2$. Geometries of the corresponding adducts are shown in **Figure 5**. The interaction with lithium leads

to significant distortion of planar aromatic structure of triphenylene. The increase of Li:PAH ratio leads to even more significant distortion. However, this effect is much less for the dimeric structures. When lithium interacts with two molecules of triphenylene, it tends to occupy the space in between the molecules first. Lithium does not interact with the central ring of triphenylene, and the maximum number of lithiums in between the molecules is 3.

The average binding energies ΔE_{Li}^B per lithium atom for $Li_x(TRI)$ and the dimers $Li_{2x}(TRI)_2$ obtained from our calculations are shown in **Table 4**. Since the binding energy represents the energy that the system produces upon interaction with a certain amount of lithium, it correlates with the enthalpy change: $\Delta E_{Li}^B \sim \Delta H$ ¹⁰. As can be seen from **Table 4**, the values of ΔE_{Li}^B for $Li_x(TRI)_1$ are significantly lower than the values of ΔH . However, the ΔE_{Li}^B is much larger for the dimeric structures. The value for $Li_2(TRI)_2$ is very close to the experimental value of ΔH . Nevertheless, ΔE_{Li}^B of $Li_8(TRI)_2$ is a bit lower than the value for $Li_4(TRI)_2$, which is different from ΔH and ΔE_{Li}^B correlation for $Li_x(TRI)$ (both the values increase upon the Li:TRI ratio increase). This result can explain the fact that $Li_{4.0}(TRI)(THF)_{123}$ has lower conductivity than $Li_{2.0}(TRI)(THF)_{123}$, meaning that the formation of the $Li_8(TRI)_2$ conductive complex is less thermodynamically favorable comparing to $Li_2(TRI)_4$.

Conclusions

Among tested $Li_n(TRI)(THF)_{123}$, the Li SES with $n = 2$ demonstrates the highest conductivity, which is almost ten times higher of the naphthalene based Li SES (Li:Naphthalene ratio = 1:1) of the same concentration in THF. For $n > 2$, the conductivity of Li SES gradually decreases until $n = 4$, however, these values are still higher of the one for naphthalene. All Li SES tested demonstrate

linear decrease of conductivity with temperature increase, similar to metals and Li SES based on ammonia, naphthalene and biphenyl.

The values of ΔS and ΔH for $\text{Li}_{2.0}(\text{TRI})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ were calculated based on OCP vs T correlation. The ΔS values are lower of those for biphenyl suggesting the molecules triphenylene based Li SES have less degrees of freedom. However, the ΔS for $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ is higher of the one for naphthalene based Li SES. The ΔS values for both $\text{Li}_{2.0}(\text{TRI})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ are higher than the values for solid state electrodes due to more degrees of freedom in a solution comparing to solid.

Based on the modeling of interactions between Li and triphenylene, binding energies of lithium to one and two molecules of triphenylene were obtained (Li:TRI ratio = 2 and 4). Based on these results, one can conclude that the unusually high conductivity of triphenylene based Li SES could be related to a conductive complex formation.

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Abbreviations

LIB, Lithium ion battery; N, Naphthalene, PAH, polyaromatic hydrocarbon; THF, Tetrahydrofuran; TRI, Triphenylene; SES, Solvated electron solution.

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FIGURES

Figure 1. The structure of naphthalene (N) and triphenylene (TRI)

Figure 2. The conductivity vs. temperature profile for $\text{Li}_x(\text{TRI})(\text{THF})_{123}$ ($x = 0.5; 1.0; 2.0; 3.0; 4.0$) and $\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$.

Figure 3. Conductivity vs. Li:TRI ratio profile.

Figure 4. The E vs T profiles of $\text{Li}_{2.0}(\text{TRI})(\text{THF})_{123}$ and $\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$ in Li/Ceramics/Li SES half-cell configurations.

Figure 5. Structures of $\text{Li}_2(\text{TRI})_1$ (top left), $\text{Li}_4(\text{TRI})_1$ (top right), $\text{Li}_4(\text{TRI})_2$ (bottom left), $\text{Li}_8(\text{TRI})_2$ (bottom right).

TABLES

Li SES	σ ($\mu\text{S/cm}$) at 295.15 K	$\sigma(T)$ ($\mu\text{S/cm}$) =
$\text{Li}_{1.0}(\text{N})(\text{THF})_{123}$	34.2	$-3.02T+920$
$\text{Li}_{0.5}(\text{TRI})(\text{THF})_{123}$	17.6	$-0.78T+248$
$\text{Li}_{1.0}(\text{TRI})(\text{THF})_{123}$	62.2	$-6.06T+1848$
$\text{Li}_{2.0}(\text{TRI})(\text{THF})_{123}$	579	$-12.07T+4133$
$\text{Li}_{3.0}(\text{TRI})(\text{THF})_{123}$	344	$-7.52T+2590$
$\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$	331	$-8.32T+2954$

Table 1. The conductivity (σ , $\mu\text{S/cm}$) values at 295.15 K (22 °C) and the equations of quasi-linear $\sigma(T)$ for the studied Li SES.

Li SES	E at 295.15 K (mV)	E(T) (mV) =	ΔS (J/(mol*K))	ΔH (kJ/mol)
$\text{Li}_{2.0}(\text{TRI})(\text{THF})_{123}$	747.2	$-2.48T+1478$	-239.3	-142.7
$\text{Li}_{4.0}(\text{TRI})(\text{THF})_{123}$	678.8	$-3.25T+1636$	-313.6	-157.9

Table 2. Open-circuit potentials at 295 K (22 °C), ΔS and ΔH of the $\text{Li}_n(\text{TRI})(\text{THF})_{123}/\text{Li}$ half-cells, $n = 2.0$ and 4.0

Type of half-cell	ΔS (JK ⁻¹ mol ⁻¹)
Li _{0.5} β (THF) _{24.7} (Biphenyl-based)	-420
Li _{1.0} β (THF) _{24.7} (Biphenyl-based)	-467
Li _{1.0} N(THF) _{24.7} (Naphthalene-based)	-290
Li _{2.0} (TRI)(THF) ₁₂₃	-239
Li _{4.0} (TRI)(THF) ₁₂₃	-316
Li _n CoO ₂ /Li	-70 < ΔS < 20
Li _n C ₆ /Li	-18 < ΔS < +62

Table 3. Entropy changes for various Li SES/Li compared with Li_nCoO₂/Li² and Li_nC₆/Li³ half-cells (0 < n < 1).

	ΔH (kJ/mol) experimental	ΔE_{Li}^B , eV	ΔE_{Li}^B , kJ mol	ΔE_{Li}^B (Dimer), eV	ΔE_{Li}^B (Dimer), kJ
$Li_2(TRI)$	-142.7	-0.67	-64.6	-1.41	-136.1
$Li_4(TRI)$	-157.9	-0.94	-90.7	-1.24	-119.6

Table 4. Calculated average binding energies ΔE_{Li}^B for $Li_x(TRI)_1$ and dimeric $Li_{2x}(TRI)_2$ (x = 2 and 4)

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