



# 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  $\pi$ -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  $\Delta S$  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 than 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.

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## 1. 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 (Fig. 1).

## 2. 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, 0.1 M 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  $\text{Li}_x(\text{TRI})(\text{THF})_{123}$ .

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

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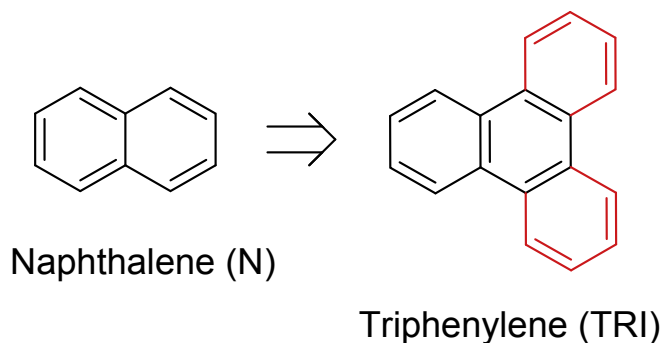


Fig. 1. The structure of naphthalene (N) and triphenylene (TRI).

### 2.1. Conductivity ( $\sigma$ ) vs. temperature ( $T$ ) measurements

Conductivity ( $\sigma$ ) 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 m and calibrated using 0.01 M 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 (see Table 1).

### 2.2. 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.

### 2.3. Modeling

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 6–31 g (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.

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

Li SES	$\sigma$ ( $\mu\text{S}/\text{cm}$ ) at 295.15 K	$\sigma(T)$ ( $\mu\text{S}/\text{cm}$ ) =
Li <sub>1,0</sub> (N) (THF) <sub>123</sub>	34.2	$-3.02T + 920$
Li <sub>0,5</sub> (TRI) (THF) <sub>123</sub>	17.6	$-0.78T + 248$
Li <sub>1,0</sub> (TRI) (THF) <sub>123</sub>	62.2	$-6.06T + 1848$
Li <sub>2,0</sub> (TRI) (THF) <sub>123</sub>	579	$-12.07T + 4133$
Li <sub>3,0</sub> (TRI) (THF) <sub>123</sub>	344	$-7.52T + 2590$
Li <sub>4,0</sub> (TRI) (THF) <sub>123</sub>	331	$-8.32T + 2954$

## 3. Results and discussion

### 3.1. Conductivity

The conductivity vs. temperature correlation for Li<sub>x</sub> (TRI) (THF)<sub>123</sub> solutions ( $x = 0.5; 1.0; 2.0; 3.0; 4.0$ ) and naphthalene based Li<sub>1,0</sub>(N) (THF)<sub>123</sub> is shown in Fig. 2. Although the conductivity of Li<sub>1,0</sub> (TRI) (THF)<sub>123</sub> is lower than the one for Li<sub>1,0</sub>(N) (THF)<sub>123</sub>, the conductivities of all the other solutions are significantly higher. The highest value of conductivity is observed for Li<sub>2,0</sub> (TRI) (THF)<sub>123</sub>. This value at 295 K (22 °C) is 17 times higher than for Li<sub>1,0</sub>(Naphthalene) (THF)<sub>123</sub> (Table 2). The conductivity of triphenylene based Li SES starts decreasing upon further increase of Li:TRI ration, however, the conductivity of Li<sub>4,0</sub> (TRI) (THF)<sub>123</sub> at 295 K is still 9.7 times higher than for Li<sub>1,0</sub>(Naphthalene) (THF)<sub>123</sub>. 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  $\pi$ -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 (Fig. 3). This pattern is very similar to diluted naphthalene and biphenyl based solutions with the formula of Li<sub>x</sub> (PAH) (THF)<sub>25</sub> [1,2].

### 3.2. 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 Li<sub>2,0</sub> (TRI) (THF)<sub>123</sub> and Li<sub>4,0</sub> (TRI) (THF)<sub>123</sub> in Li/Ceramics/Li SES half-cell configurations are shown in Fig. 4. The enthalpy changes (Table 2) and the entropy changes of the half-cell were calculated using the following equations ( $n = 1$  for lithium,  $F =$  Faraday constant): [7]

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

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

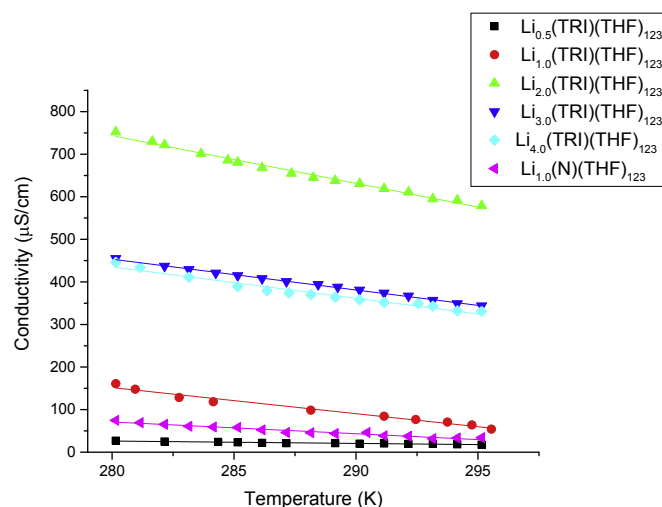


Fig. 2. The conductivity vs. temperature profile for Li<sub>x</sub> (TRI) (THF)<sub>123</sub> ( $x = 0.5; 1.0; 2.0; 3.0; 4.0$ ) and Li<sub>1,0</sub>(N) (THF)<sub>123</sub>.

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