Electrochemical Properties of Anthracene-Based Lithium-Solvated Electron Solutions

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ABSTRACT: The conductivity and open-circuit voltage (OCV) of lithium-solvated electron solutions (LiSESs) based on anthracene in tetrahydrofuran were studied by both experimental measurements and density functional theory calculations with a range-separated functional based on the M06 form and the Solvation Model based on Density (SMD). The OCV was found to decrease with increasing temperature and the ratio of lithium to anthracene. The enthalpy change (ΔH) of LiSESs was the internal energy change of the cell reaction. The conductivity of LiSESs exhibited a weakly metallic-like behavior. The electron transport was facilitated by molecular collisions promoted by the formation of dimeric structures as intermediates. The conductivity of LiSESs at 295.15 K presents positive correlation with the entropy change (ΔS) associated with the variation in the ratio of lithium to poly-aromatic hydrocarbon, including p-terphenyl, anthracene, and triphenylene.

1. INTRODUCTION

Since the first fabrication of the lithium ion battery in the 1970s, it has quickly become an important power source for portable devices. Researchers have made a lot of efforts to improve the performance of lithium-based batteries and one long-standing problem is the anode material. Current research interests mainly focus on solid-state and semisolid-state anode materials such as graphite, carbonaceous materials,1–3 and alkali metals such as lithium.4,5 However, the semisolid lithium flow cells have very poor conductivity so that large quantity of additives was required to improve the conductivity.6 Solid anode materials such as metallic lithium have some associated safety problems as well as slow recharge rate. A potential alternative anode material was the lithium-solvated electron solution, a liquid-state anode material where metallic lithium is dissolved in tetrahydrofuran (THF) solutions of poly-aromatic hydrocarbons (PAHs). It has been experimentally verified that lithium dissolved in THF solution of biphenyl and naphthalene could be used as the anode material in a cell to replace solid-state graphite,7 with remarkable electrochemical properties of biphenyl8 and naphthalene9-based LiSESs. The main feature of LiSESs is that they show weak metallic-like conductivity behavior—the conductivity of LiSESs decreases with increasing temperature. In addition, studies on interactions between lithium and biphenyl and naphthalene have shown remarkable energy storage capacity, where the lithium atoms bind to PAH through charge-transfer processes.10,11 In our recent work,12 we investigated the open-circuit voltage (OCV) and conductivity of triphenylene-based LiSESs and reported the entropy changes of LiSESs when varying lithium concentration. In this work, the electrochemical properties of anthracene-based LiSESs are characterized by OCV and conductivity measurements, in comparison with enthalpy change associated with binding lithium atoms to anthracene monomer, and the entropy change (ΔS) associated with the variation in the ratio of lithium to PAH.

Received: December 25, 2018
Accepted: February 19, 2019
Published: March 4, 2019

DOI: 10.1021/acsomega.8b03621
ACS Omega 2019, 4, 4707−4711
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2. RESULTS AND DISCUSSIONS

2.1. OCV, Entropy, and Enthalpy of the LiSESs. In the half-cell experiment measurement of OCV of anthracene-based LiSESs, metallic lithium is used as the reference electrode. On the lithium electrode side, lithium is oxidized into Li+, whereas on the LiSES electrode side, anthracene molecules receive electrons, binding to Li+ which is transported through Li+-conducting membrane.

This process is modeled by the lithium anthracene complex illustrated in Figure 1a. The 2s electron of lithium atom is transferred to anthracene molecule. Various complex structures are obtained by locating lithium atom at different positions. The average binding energy per lithium atom of the system is determined by

$$E_b = -(E_{\text{complex}} - (E_{\text{anthracene}} + n \times E_{\text{Li}}))/n$$

(1)

With one lithium atom binding to an anthracene molecule, the structure with lithium atom above the center ring (9, 10-position) of anthracene is more stable, which is consistent with the reported higher reactivity of the center ring of anthracene molecule. The center ring has the highest aromaticity because of the superposition of the resonance effect of its own and the double induction effect from adjacent resonating ring (one at a Kekulé structure as shown in Figure 1a). This provides one geometric account for the highest nucleus-independent chemical shifts of central ring. When the second lithium atom is added, the anthracene molecule would bend because of stronger interaction with lithium atoms. When lithium atoms are positioned at the edges of the anthracene molecule, the binding strength is smaller than the case where one lithium is at the middle and the other is at the edge of anthracene. It is also noticed that the binding energy of the structures with lithium atom positioned on the different sides of the anthracene molecule are higher than that of other configurations. The most energetically stable structure is found to be the structure with one lithium atom above the central ring and the other below the side ring. The binding energy per lithium atom in gas phase is 0.2 eV higher than the value reported by Ishikawa et al. Ishikawa used Lee–Yang–Parr correlation functional (B3LYP), whereas M06 functional developed by Zhao & Truhlar is used in this work. The average binding energy increases when the second lithium atom is incorporated. This is consistent with the larger enthalpy change determined from experiment when the ratio of lithium to anthracene increases from 1 to 2.

The OCV of anthracene-based LiSESs was measured with metallic lithium as its reference electrode in half-cell experiment. OCV ($V_{\text{ocv}}$) is determined in terms of the lithium chemical potential difference between the half-cell ($\mu_{\text{hc}}$) and the reference electrode ($\mu_{\text{ref}}$) as

$$V_{\text{ocv}} = \frac{\mu_{\text{hc}} - \mu_{\text{ref}}}{zF}$$

(2)

where $z$ indicates the charge transferred in the cell reaction and $F$ is the Faraday’s constant. For a LiSES half-cell with lithium metal as the reference electrode, $z$ was set to be 1 because lithium loses one electron during cell reaction. The lithium chemical potential difference is the free-energy change of
electrode materials with different lithium content with respect to metallic lithium.\textsuperscript{17,18} Thus, the OCV could be written as a function of free-energy change of the cell reaction through the Nernst equation

\[
V_{\text{OCV}} = -\frac{\Delta G}{zF} = -\frac{\Delta H - T\Delta S}{zF}
\]

(3)

$\Delta H$ is the enthalpy change and $\Delta S$ is the entropy change of the cell reaction. The entropy change can be computed from the temperature dependence of the OCV as presented in Figure 1b. At a temperature of 25 °C, the OCV of the LiSES is measured to be 937.0 mV for the ratio of Li to anthracene ratio as 1:2, 903.9 mV for 1:1, and 897.7 mV for 2:1. Within the temperature range of 11−26 °C, the LiSES with a Li to anthracene ratio of 1:2 has the highest OCV. The OCV decreases with increasing temperature for all LiSESs with different ratios of lithium to anthracene, which can be used to compute the entropy change as shown in eq 3. The formation of lithium−anthracene complex via binding lithium atoms to anthracene molecules reduces the degree of freedom and resulting in a negative entropy change. In this temperature range, the OCV of the LiSES decreases with increasing lithium concentration can be understood from two aspects: the ideal limit of lithium concentration is 100%, which means no free energy difference due to the reference electrode is pure lithium; the other aspect is considering that the increasing lithium concentration will lead to larger entropy reduction as shown in Figure 1b.

Using eq 3, the enthalpy changes of the LiSES during cell reactions are determined to be $-1.35$, $-1.33$, and $-1.43$ eV for the ratio of Li to anthracene as 0.5, 1.0, and 2.0, respectively. The enthalpy change of the cell reaction refers to the internal energy change which can also be obtained through theoretical computation. We employ the M06 functional\textsuperscript{16} with 6-31g(d,p) basis set and SMD model\textsuperscript{22} to compute the enthalpy change in anthracene-based LiSESs. The computed enthalpy change is in good agreement with the experimental results as shown in Figure 1c. For all LiSESs, the absolute values of our computed enthalpy change are larger than experimental data. The discrepancy could come from two sources. First, the complex structures are not identical to the real ones in LiSESs. Second, the electrolyte might interact with the reference electrode, that is, metallic lithium, in the experiment. It has been reported that LiPF\textsubscript{6} in 1:1 ethylene carbonate (EC)/ethyl methyl carbonate (EMC) solvent would be slowly decomposed into LiF and PF\textsubscript{5}, which could form adduct with the solvent molecules and triggers a series of subsequent reactions.\textsuperscript{23−25} This would alter the chemical potential of the reference electrode, thus affects the measured data of enthalpy change.

2.2. Conductivity of the LiSES. The carrier transport in the LiSES is enabled by the collision processes among anthracenes and lithium-bounded anthracenes in the solution. During the collision, various dimeric structures could be formed as shown in Figure 2a. For instance, one anthracene can collide with the complex of lithium and anthracene, resulting in one dimeric structure where the lithium atom is sandwiched in between two anthracenes with a separation of 3.6 Å. The binding energy turns out to be the highest value when the ratio of lithium to anthracene is 1:1. Compared with the complex with monomeric anthracene, the complex with...
dimeric anthracenes exhibits much higher binding energy. Similarly, the electron transport during molecular collisions is an important conducting process in the solution, and the process is possibly performed through the formation of dimeric structures. To investigate the mechanism of electron transport among anthracenes in LiSESs, the conductivity of 0.1 M anthracene-based LiSESs with different ratios of lithium to anthracene is measured under different temperatures as presented in Figure 2b.

When the ratio of lithium to anthracene is 1:2, the excess of anthracene could form dimers. The heterogeneity of the solution is very high. Correspondingly, the orientation of dimers is not well ordered, leading to poor conductivity. When raising the temperature, more disorder is anticipated, and therefore, conductivity decreases further. Interestingly, when the ratio of lithium to anthracene is 1:1, the complex with dimeric anthracenes reaches to the maximal value, which could promote better alignment of these dimers. Therefore, the conductivity is the highest. Under this circumstance, the disorder caused by increasing temperature is stronger than other cases. When the ratio of lithium to anthracene increases to 2:1, the excess lithium will generate clusters among complexes. Again, the system is not well ordered in terms of orientation of dimers. Thus, the conductivity becomes poor again. The LiSESs have a similar conductivity for the ratio of lithium to anthracene as 0.5:1 and 2:1. The conductivity of all LiSESs decreases when temperature increases, similar to metallic systems. This temperature-dependent conductivity is also observed in other LiSESs based on triphenylene, p-terphenyl, and ammonia. The conductivity is first enhanced and then suppressed when more lithium is added into the solutions as shown in Figure 2c. This scenario is supported by the nice correlation between conductivity and binding energy of the dimeric structures as presented in Figure 2c. A similar correlation was also found in LiSESs based on triphenylene.12

The conductivity of LiSES at 295.15 K presents positive correlation with the entropy change (ΔS) associated with the variation in the ratio of lithium to PAH, including p-terphenyl, anthracene, and triphenylene as shown in Figure 3. The conductivity of p-terphenyl-based LiSES increases linearly with the entropy change caused by varying lithium content, so do triphenylene and anthracene. When more lithium atoms are incorporated in the LiSES, the entropy change in the cell reaction becomes more negative. This is due to the fact that the formation of more tightly bound complex of lithium and anthracene reduces more degrees of freedom of the system. Importantly, tightly bound complex disturbs the alignment of PAH, leading to more disorder in the geometric orientation. The implication is that the entropy change of cell reaction and entropy change of dimeric structure spatial distribution are negatively correlated in LiSESs. Thus, the conductivity of LiSESs will decrease as the entropy change of cell reaction becomes more negative, when increasing the ratio of lithium to PAH.

3. CONCLUSIONS

The interaction between lithium and anthracene molecules, quantified by the enthalpy change, determines the OCV of LiSESs. The conductivity exhibits metallic-like behavior, where the conductivity of the solutions decreases with raising the temperature. The clear correlation between the change of conductivity and the binding affinity of dimeric lithium and anthracene complex for different ratio of lithium to anthracene suggests that charge carriers transport in LiSESs through molecular collision facilitated by dimer formation process. Interestingly, a general positive correlation between the conductivity and entropy change is observed in three types of PAH-based LiSESs, which could hold for other PAH-based LiSES as well.

4. COMPUTATIONAL AND EXPERIMENTAL METHODS

4.1. Computational Method. Density functional theory based calculations with the range-separated functional based on the M06 form,16 which includes the van der Waals force, have been performed with the 6-31g(d,p) basis set to optimize the geometries and calculate the binding energies of various structures between lithium atoms and anthracene molecules. The solvent effect was modeled with SMD model.22

4.2. Preparation of LiSES Based on Anthracene. Reagents were purchased from Sigma-Aldrich and used as received. LiSES samples were prepared inside an argon-filled glove box using anhydrous THF as the solvent. The 0.1 M solutions were made by dissolving anthracene in THF with molar ratio 1:123 (the volume expansion due to anthracene dissolution was neglected). Various amounts of lithium metal were then added to the solution to form anthracene-based LiSES with a Li−anthracene ratio of 0.5, 1.0, and 2.0.

4.3. Conductivity Measurements. Conductivity measurements of the anthracene-based LiSESs were carried out at various temperatures ranging from 1 to 23 °C using a modified procedure previously described for naphthalene-based LiSESs.9 TetraCon 325 Standard conductivity cell probe that utilizes the four-electrode measuring principle with the measurement range of 1 μS/m to 2 S/cm was used for conductivity measurements. The probe was attached to a Cond 3310 meter and calibrated using a 0.01 M KCl solution. A sealed tube containing LiSES with the probe dipped into the solution was measured at different temperatures as shown in Figure 2b.

Figure 3. Conductivity at 295.15 K and entropy change (ΔS) of cell reaction of 0.1 M anthracene, triphenylene,12,26 and p-terphenyl10-based LiSESs. The ratio in the parenthesis refers to the ratio of Li to PAHs.

DOI: 10.1021/acsomega.8b03621
ACS Omega 2019, 4, 4707−4711
tube was exposed to ambient temperature. The conductivity of the solution was measured and recorded upon heating up the tube.

**4.4. OCV Measurements.** Metallic lithium was immersed in 1 M LiPF$_6$ in the EC/EMC electrolyte solution and served as the reference electrode during the OCV measurement for LiSEs. A Li$^+$-conducting ceramic membrane was used as a separator between the lithium metal electrode and LiSEs electrode. The OCV was measured at the temperature range of 11–26 °C. From the temperature dependence of OCV, the entropy and enthalpy changes to be determined for the half-cell could be determined.  

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The work is supported in part by the Society of Interdisciplinary Research (SOIRE), HKUST Grants (IGN17SC04; R9418), Ministry of Education (Singapore) through Academic Research Fund Tier 2 Grant (MOE2013-T2-2-002), and Tianneng Power International. The authors also thank C. Wu and F. Zhou for stimulating discussions.

**REFERENCES**

(1) Chen, J. Recent progress in advanced materials for lithium ion batteries. Materials 2013, 6, 156–183.

(2) de las Casas, C.; Li, W. A review of application of carbon nanotubes for lithium battery anode material. J. Power Sources 2012, 208, 74–85.

(3) Scrosati, B.; Garche, J. Lithium batteries: Status, prospects and future. J. Power Sources 2010, 195, 2419–2430.

(4) Lu, Y.; Goodenough, J. B. Rechargeable alkali-ion cathode-flow battery. J. Mater. Chem. 2011, 21, 10113–10117.

(5) Wang, Y.; He, P.; Zhou, H. Li-redox flow batteries based on hybrid electrolytes: At the cross road between Li-ion and redox flow batteries. Adv. Energy Mater. 2012, 2, 770–779.

(6) Park, M.; Zhang, X.; Chung, M.; Less, G. B.; Sastry, A. M. A review of conduction phenomena in Li-ion batteries. J. Power Sources 2010, 195, 7904–7929.

(7) Yazami, R. Hybrid electrochemical generator with a soluble anode. U.S. Patent 2,010,014,121,1A1, 2010.

(8) Tan, K. S.; Grimsdale, A. C.; Yazami, R. Synthesis and Characterization of Biphenyl-Based Lithium Solvated Electrons Solutions. J. Phys. Chem. B 2012, 116, 9056–9060.

(9) Tan, K. S.; Yazami, R. Physical-Chemical and Electrochemical Studies of the Lithium Naphthalene Diol. Electrochem. Acta 2015, 180, 629–635.

(10) de la Viuda, M.; Yus, M.; Guijarro, A. On the Nature of Lithium Biphenyl in Etheereal Solvents. A Critical Analysis Unifying DFT Calculations, Physicochemical Data in Solution, and a X-ray Structure. J. Phys. Chem. B 2011, 115, 14613–14616.

(11) Lee, J. S.; Krasnokutski, S. A.; Yang, D.-S. High-resolution electron spectroscopy, preferential metal-binding sites, and thermochemistry of lithium complexes of polycyclic aromatic hydrocarbons. J. Chem. Phys. 2011, 134, 024301.