A conductivity study of preferential solvation of lithium ion in acetonitrile-dimethyl sulfoxide mixtures

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ABSTRACT

The electrical mobility of $LiPF_6$ in acetonitrile–dimethyl sulfoxide (ACN–DMSO) mixtures, a potential electrolyte in oxygen cathodes of lithium-air batteries, has been studied using a very precise conductance technique, which allowed the determination of the infinite dilution molar conductivity and association constant of the salt in the whole composition range. In the search for preferential Li^+ ion solvation, we also measured the electrical conductivity of tetrabutylammonium hexafluorophosphate ($TBAPF_6$), a salt formed by a bulky cation, over the same composition range. The results show a qualitative change in the curvature of the $LiPF_6$ molar conductivity composition dependence for ACN molar fraction ($x_{ACN}) \sim 0.95$, which was not observed for $TBAPF_6$. The dependence of the measured Li/Li^+ couple potential with solvent composition also showed a pronounced change around the same composition. We suggest that these observations can be explained by Li^+ ion preferential solvation by DMSO in ACN–DMSO mixtures with very low molar fractions of DMSO.

1. Introduction

Li-ion batteries have conquered the market of portable electronics after their successful commercialization by Sony in the early 1990s. However, in recent years numerous efforts have been performed in order to meet a global energy challenge and develop Li-based batteries that would possess a superior power density to that of Li-ion, such as Li-S or Li-air [1]. Li-air batteries are theoretically very promising and this technology has recently gained a wide scientific attention with an increasing number of investigations conducted each year [2–4].

Among the research concerning the potentially interesting electrolytes for lithium batteries, transport studies are of great interest and importance. Numerous studies of transport properties of several electrolyte systems for Li-ion batteries are nowadays available [5–7]. However, it has been shown that typical electrolyte systems employed in Li-ion batteries (based on organic carbonates and ethers) are not appropriate for Li-air batteries due to the electrolyte decomposition by the oxygen reduction reaction (ORR) intermediates and/or products [8–16]. Thus, more information on transport properties in other electrolyte systems for Li-air batteries is

needed. Recent studies have suggested that dimethyl sulfoxide (DMSO) seems to be a promising candidate for Li-air batteries [17–19]. Using Infrared spectroscopy, we failed to detect dimethyl sulfone in the electrolyte resulting from the nucleophilic attack by the electrogenerated superoxide radical anion [20]. However, there is a controversy on the stability of DMSO in contact with Li_2O_2 [21,22]. Sharon et al. [21] pointed out that DMSO may not be a suitable solvent for rechargeable $Li - O_2$ cells due to its oxidation by reactive oxygen species and lithium oxides. McCloskey et al. [23] have shown that the balance of oxygen consumed in the ORR and that evolved in the oxygen evolution reaction (OER) during charging is always less than 0.9 due to the heterogeneous chemical reaction of the solid peroxide with the electrolyte or the carbon cathode. However, DMSO exhibits unusual properties related to the ORR that is stabilization of the intermediate O_2^- anion, which does not occur in other solvents [18]. We have reported [24], that soluble superoxide radical anions can be detected at a rotating ring disk electrode (RRDE) system in lithium solutions of acetonitrile (ACN) containing 0.1 M DMSO ($x_{ACN} = 0.995$), while no evidences of soluble O_2^- are observed in lithium acetonitrile solutions. We have suggested that those observations could be due to the preferential solvation of Li^+ cation by DMSO molecules that in turn prevents the disproportion of lithium superoxide ($2 O_2Li \rightarrow Li_2O_2 + O_2$). In order to test this hypothesis, in this work, we have studied the ionic conductivity of lithium hexafluorophosphate ($LiPF_6$) in comparison to

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tetrabutylamonium hexafluorophosphate (TBAPF$_6$) in ACN–DMSO mixtures in the whole composition range. These results were complemented with measurements of Li/Li$^+$ electrode potential as a function of the composition of the ACN–DMSO mixture.

2. Experimental

2.1. Materials

Anhydrous dimethyl sulfoxide (DMSO) $\geq$99.9% (SIGMA–ALDRICH), acetonitrile (ACN) (SIGMA–ALDRICH), tetrabutylammonium hexafluorophosphate (TBAPF$_6$) for electrochemical analysis, $\geq$99.0% (FLUKA), and lithium hexafluorophosphate (LiPF$_6$) battery grade $\geq$99.99% trace metals basis (ALDRICH), were stored in an argon-filled MBRAUN glove box with oxygen content $\leq$0.1 ppm and water content <2 ppm. DMSO and ACN were dried for several days over molecular sieves 3A (SIGMA–ALDRICH); TBAPF$_6$ and LiPF$_6$ were used as received. All solutions were prepared inside the glove box and the water content was measured using Karl Fisher coulometric titration (831 KFCoulometer (Metrohm)). All solutions were found to contain less than 20 ppm of water at the beginning and less than 30 ppm of water at the end of conductivity measurements.

2.2. Redox potential of the Li/Li$^+$ electrode in DMSO/ACN mixtures.

The anode material for the Li-air battery is lithium metal; therefore it is common to refer to the Li/Li$^+$ scale when presenting electrochemical studies of the cathode reaction (oxygen reduction reaction ORR and oxygen evolution reaction OER). However, Li metal itself is rarely used as a reference electrode, but typically other non-aqueous reference electrodes are used, which are referred to Li/Li$^+$ by measuring its potential versus lithium wire or calibrating with ferrocene couple. However, while referring an electrode to the lithium wire, it should be taken into account that the potential of the Li/Li$^+$ couple depends on the electrolyte in which it measured since Li$^+$ solvation energy depends notably on the solvent.

In this work, we studied the Li/Li$^+$ potential dependence on solvent composition in ACN–DMSO mixtures by resorting to the cell:

Li$_2$Mn$_2$O$_4$/LiMn$_2$O$_4$/1 M LiPF$_6$ (DMSO)//0.1 M LiPF$_6$ (ACN–DMSO)/Li

The reference Li$_2$Mn$_2$O$_4$/LiMn$_2$O$_4$ electrode was prepared as described:

1) LiMn$_2$O$_4$ synthesis: Li$_2$CO$_3$ and MnO$_2$ were mixed in a molar relation 0.51:2, grounded, pressed and heated at 350 °C for 12 h and at 800 °C for 24 h.
2) Li$_2$Mn$_2$O$_4$ synthesis: equimolar amounts of LiMn$_2$O$_4$ and LiI were mixed and placed in a vacuum oven at 80 °C overnight.
3) Equimolar quantities of LiMn$_2$O$_4$ and Li$_2$Mn$_2$O$_4$ were mixed with Carbon black (10% of total mixture weight) and PVDF binder (10% of total mixture weight) and dissolved in an appropriate organic solvent to make an ink.
4) A Pt wire was covered with the ink, and placed in a fritted glass compartment containing 1 M LiPF$_6$ in DMSO solution.

All measurements were performed inside the glove box.

The liquid junction potential between the 1 M LiPF$_6$ (DMSO) solution and the 0.1 M LiPF$_6$ solution in the studied ACN–DMSO mixture was calculated as:

$$E_j = (t_+ - t_-)\frac{RT}{F}\ln\left(\frac{a_1}{a_2}\right) \tag{1}$$

where t_+ and t_- are the transport numbers of the cation and anion, respectively and a_1 and a_2 the activities of the salt that form the liquid junction. We approximated the electrolytes activities with the concentration of the salt solutions considering this correction is minor. Based on conductivity studies [25–31], the transport numbers of Li$^+$ in ACN and DMSO are 0.39 and 0.36, respectively. The calculated liquid junction potential varies between 0.013 V in ACN, and 0.017 V in DMSO and can be neglected over all the range of ACN–DMSO compositions.

It should also be considered that the Li$_2$Mn$_2$O$_4$/LiMn$_2$O$_4$ reversible reference electrode is immersed in DMSO, while the Li/Li$^+$ electrode is in the ACN–DMSO mixture. Thus, an additional potential difference exists on the interface of DMSO with the corresponding ACN–DMSO mixture, due to the variation in the dielectric constant of the mixtures. In order to correct the measured potential due to the interface between the DMSO reference electrode and the ACN–DMSO mixture, we have also calibrated the Li$_2$Mn$_2$O$_4$/LiMn$_2$O$_4$ reference electrode with the ferrocene Fe(C$_5$H$_5$)$_2$ – ferrocenium couple for all the solutions of interest. The calibration was performed by measuring cyclic voltammograms in 0.1 M LiPF$_6$ + 5–10 mmol Fe(C$_5$H$_5$)$_2$ in ACN–DMSO solutions, using a standard 3-electrode electrochemical cell with a Pt working electrode, a Li$_2$Mn$_2$O$_4$/LiMn$_2$O$_4$ reference electrode and a carbon rod counter electrode.

2.3. Viscosity of ACN–DMSO mixtures.

Owing to the significant difference between the literature reported viscosity values of the mixtures [32,33] (up to 20% difference for some compositions), we measured the viscosities of ACN–DMSO mixtures in the whole composition range with Cannon–Fenske (Ostwald modification) viscometers size 25 (0.5–2 mPa s) and size 50 (0.8–4 mPa s), calibrated with water.

For viscosity determinations, viscometers were filled with the solution of interest inside the glovebox, sealed with Teflon caps, taken out of the glove box and thermostated in a water bath at 298.15 ± 0.05 K. Then, the viscometers were opened and measurements were performed immediately to avoid water contamination.

2.4. Conductivity of LiPF$_6$ and TBAPF$_6$ in ACN–DMSO mixtures.

An air-tight glass conductivity cell with a mixing bulb and platinized platinum electrodes was used to determine the conductivity of LiPF$_6$ and TBAPF$_6$ in ACN–DMSO mixtures as a function of electrolyte concentration ($10^{-5} – 10^{-3}$ M) and solvent composition. Conductivity measurements for LiPF$_6$ were performed for ACN–DMSO mixtures with ACN molar fractions (x_{ACN}) = 0.000, 0.192, 0.373, 0.453, 0.586, 0.697, 0.798, 0.898, 0.947, 0.968, 0.995, and 1.000. Measurements for TBAPF$_6$ were performed for x_{ACN} = 0.269, 0.492, 0.754, and 0.960.

The cell constant, k_{cell} = 0.0710 ± 0.0008 cm^{-1} at 298.15 K, was determined using a standard KCl aqueous solution of known specific conductivity [34].

The conductivity measurements were performed according to the following protocol: first, the conductivity cell was filled with the solvent inside the glove box, by weighting the corresponding amounts of ACN and DMSO to obtain the desired composition. Then, the cell was transferred to an oil bath thermostatized at 298.15 ± 0.08 K and after reaching thermal equilibrium, the solvent resistance was measured. Afterwards, increasing weighted amounts of a stock solution of LiPF$_6$ or TBAPF$_6$, prepared inside the glove box, in an ACN–DMSO mixture of equal composition, were added. Additions were transferred from a stock solution containing vessel to the conductivity cell (both air-tight and equipped with septum) with the use of a syringe. The resulting solution was homogenized by manual stirring; after reaching a new thermal equilibrium, the solution resistance was determined.