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The Correct Assessment of Standard Potentials of Reference Electrodes in Non-Aqueous Solution

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The challenges facing metal-air batteries have prompted fundamental studies of non-aqueous electrochemistry. However it appears that contributors in the field are not aware that the potentials of Li/Li^+, Na/Na^+, K/K^+, and Mg/Mg^{2+} electrodes depend on the nature of solvent due to the cation solvation. Therefore, it is imperative to define a clear potential scale that can be correlated in different solvents. Here we report on the strong effect of the solvent on the Li/Li^+ redox potential and discuss the use of the ferrocene/ferrocenium couple as internal or external standard for the measurements in non-aqueous solvents in lithium-ion and lithium-O_2 battery systems.

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The Li-air or Li-O_2 system has captured a scientific attention worldwide due to its high theoretical energy density, however many challenges in the electrochemistry of this system still remain to reach commercialization.[1–4] Those challenges have given rise to a fundamental understanding of the oxygen reduction reaction (ORR) mechanistic paths in lithium containing aprotic solvent systems. Interestingly, almost all electrochemical measurements relevant to the Li-air battery in the literature report a potential scale versus Li/Li^+ potential, very often without specifying the solvent, electrolyte salt and lithium concentration.

Unlike in aqueous electrochemistry where the normal hydrogen electrode potential is the reference electrode of choice, in the lithium battery community the electrode potentials are referred to the Li/Li^+ system since in a lithium battery either the anode is Li metal or lithium intercalated in graphite with a redox potential very close to the metal Li/Li^+ electrode.

Due to the strong solvation of the small lithium cation and the different electron donor capacity of different solvents, the electrode potential of Li/Li^+ couple strongly depends on the solvent used and it could vary by as much as half of a volt between dimethyl sulfoxide and acetonitrile.[5]

Furthermore, in many reports while the potential scale is referred versus the Li/Li^+, Li metal is not actually used as the reference electrode, but a different reference electrode such as Ag/Ag^+ is employed and then converted into the Li/Li^+ scale often without specifying how this was done.

Current Status

Browsing through the Li-air literature we can find that in 2009 Laoire et al. used aqueous Ag/AgCl reference electrode and repored their data versus this reference. However they also indicated that Ag/AgCl gives a potential of 2.93 V versus Li/Li^+, as measured using a Li foil reference electrode in a $LiPF_6$ solution in organic carbonates.[6] This is an example of the very rare case in the Li-air literature, where the results were reported versus actual reference employed as we can see later since almost all the literature refer to the Li/Li^+ scale. In 2010, the same authors used the Pt mesh as the reference electrode and reported their data versus Li/Li^+. They argued that the Pt electrode was calibrated with reference to the ferrocenium ion/ferrocene couple in each electrolyte studied, which in turn was calibrated to the Li/Li^+ scale in ethylene carbonate/dimethyl carbonate based electrolyte.[7] Allen et al.[8] reported their studies in ionic liquid and employed as reference an electrode that consisted of a silver wire immersed in a 0.1 M $AgCF_3SO_3$ solution and converted the potentials to the Li/Li^+ reference electrode by measuring the potential difference of the Ag/Ag^+ electrode against a Li foil without specifying the solution. In 2013 Trahan et al.[9] reported studies of DMSO-based electrolyte for Li-air battery using a silver wire contained in a glass jacket filled with the working electrolyte plus a 10 mM addition of silver nitrate salt as a reference electrode. They reported a potential of 3.60 V versus Li/Li^+ by calibrating their reference in the 1 M $LiPF_6$/DMSO solution. Notably, the Baltruschat's group have used the Ag/Ag^+ reference electrode (silver wire immersed in a solution of 0.1 M $AgNO_3$ in the solvent used to prepare the electrolyte) and reported their values versus this reference.[10] Bruce's group, in turn, employed a reference electrode based on $LiFePO_4$ and mentioned that the Li_xFePO_4 reference potential was corrected to Li/Li^+ by subtracting 3.45 V[11] (data found in the article's supplementary material). The group of Gasteiger reported studies with $PYR_{14}TFSI$ ionic liquid using Ag/Ag^+ reference electrode and calibrated versus Li/Li^+ electrode (Li metal in $Pyr_{14}TFSI$ with 0.2 M LiTFSI with a value of 3.160 ± 0.002 V[12]).

After extensive literature overview we can highlight some important aspects:

1) With very few exceptions[6,10] most of the Li-air literature refers the electrode potentials to the Li/Li^+ potential scale.
2) In almost all the literature the Li/Li^+ electrode has not been used as the actual reference electrode, but a variety of reference electrodes such as Ag/AgCl, Ag/Ag^+, Ag wire, Pt mesh quasireference, $LiMn_2O_4/Li_2Mn_2O_4$, etc. have been employed.
3) The electrode potential measured vs. a reference electrode used in the experiment was later converted to Li/Li^+ scale by measuring the potential between the reference and Li foil submerged in the same electrolyte used in the experiments (best case scenario) or a different solvent (for example organic carbonate), or without the indication of the solvent used at all.
4) Very often in the literature the Li^+ concentration and solvent for Li/Li^+ reference are not reported, thus indicating that many people in the field are not aware that the potential of Li/Li^+ is highly dependent on the solvent of the lithium electrolyte.

Probably one of the best known Li/Li^+ potential values is -3.04 V vs. NHE in the aqueous solution as can be found in most tables of standard electrode potentials. As it is well known metallic lithium reacts with water, and the potential is measured by using dilute lithium amalgam, which is stable in water.

The lithium electrode potential strongly depends on the solvent-electrolyte interaction since the Li^+-ion solvation energy dominates the potential value. Without going deeply into the thermodynamics, we can assume that for the reaction

$$\mathrm{Li} = \mathrm{Li}^{+}{}_{(\mathrm{solv})} + \mathrm{e}$$

in two different solvents, the difference between the electrode potentials is proportional to the difference between the Gibbs free energies

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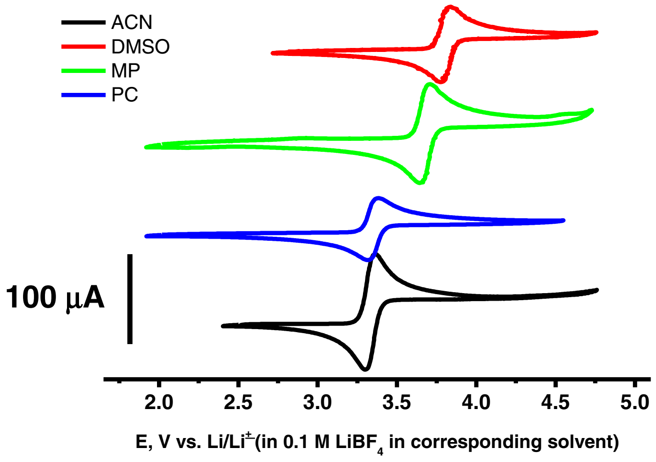

Figure 1. IR drop corrected cyclic voltammetries performed in the solution containing 10 mM ferrocene and 0.1 M $LiBF_4$ in ACN (acetonitrile), DMSO (dimethyl sulfoxide), MP (1-Methyl-2-pyrrolidinone) and PC (propylene carbonate). Working electrode: Pt, counter electrode: PT mesh, reference electrode: Li, scan rate 100 mV/s.

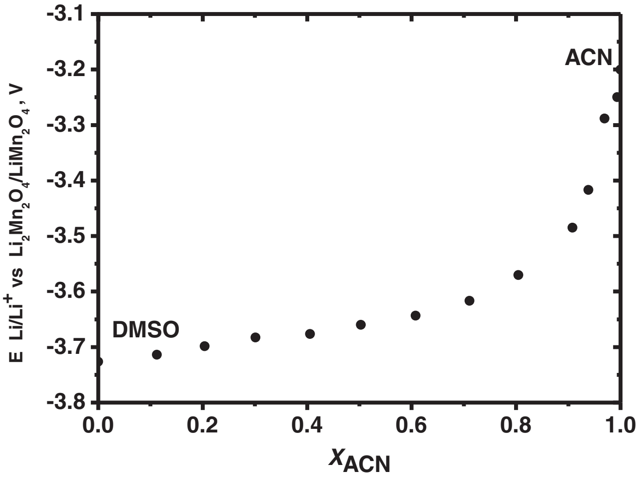

Figure 2. Li/Li$^+$ electrode potential vs. Li$^+$ reversible electrode as a function of ACN molar fraction in ACN–DMSO mixtures (taken from Ref. 5).

of solvation in those two solvents: $\Delta G = -nF\Delta E$. It is well know that for the small ion such as Li$^+$ the solvation energy may vary strongly from solvent to solvent. This is also the case for the different cations: Na$^+$, K$^+$ and Mg^{2+}, however with a smaller ΔE difference for a larger size cation (lower difference in solvation energies). That is why in 1947 Pleskov suggested to use the Rb/Rb$^+$ electrode as a reference for non-aqueous solvents; however it was found later by Koepp et al. in 1960 that even for such big cation as Rb$^+$ the difference in solvation energies could not be neglected (cited in IUPAC report[13]).

In 1983 the issue of reporting electrode potentials in non-aqueous solvents was already recognized and the IUPAC recommended to use of ferrocene/ferrocenium ion and bis (biphenyl)chromium(I)/bis(biphenyl)chromium(O) redox couples as stable internal reference.[13] Those two redox couples represent the best known solvent independent redox systems due to big size and delocalized charge, thus the solvating energies would vary very slightly in different solvents. Kwabi et. al have recently reported the use of decamethyl ferrocene to determine the redox potential of O_2/O_2^- and Li/Li$^+$ in different non aqueous solvents.[14]

We have measured the cyclic voltammetry of the ferrocene/ ferrocenium redox couple versus Li metal immersed in 0.1 M Li$^+$-containing electrolyte solutions in different aprotic organic solvents. Since it is very well documented that a Li foil in contact with acetonitrile will spontaneously react with the solvent to form a variety of products, we have carried out the measurements in a short time after immersion of the lithium foil into the electrolyte. This was only done in order to get a relative comparison of the ferrocene redox potential in different solvents and it is not recommended to use lithium metal directly as a reference electrode in contact with these solvents.

The results are presented on the Figure 1. As can be seen from the figure, the reversible ferrocene/ferrocenium couple is observed with a potentials shift varying in different solvents and reaching 0.5 V difference between ACN and DMSO. Assuming the potential of ferrocene couple is not affected by the solvent due to small solvation contribution, it is concluded that this variation is due to the shift in the “reference” Li/Li$^+$ electrode potential in each solvent.

Another interesting case is the mixed solvent electrolyte, i.e. DMSO-ACN. The estimation of the Li/Li$^+$ potential in that case is not trivial. It has been shown both experimentally[5] and theoretically,[15] that DMSO-ACN mixtures do not follow what would be expected for a regular solution: For example in 80% of ACN and 20% of DMSO (molar fractions), the Li/Li$^+$ potential value is closer to that in pure DMSO, than in pure ACN (see Figure 2). This is explained by the preferential solvation of Li$^+$ cations by DMSO molecules even in the large excess of ACN.

Another aspect that deserves consideration is the liquid junction potential due to different salt concentrations and solvents in the working solution and at the jacketed reference electrode electrolyte.

In mixtures of solvents it should be considered the contribution to the electrode potential from the different solvent´s dielectric constant when two different solvents are used in the reference electrode and working solution. We have shown a difference of about 40 mV in the liquid junction potential when using the DMSO-based reference electrode solution and the working solutions based either on ACN or DMSO; and have found that this potential difference is proportional to the inverse dielectric constant of the solution.[5]

Future Needs and Prospects

After bringing up these important points, we would like contribute the following suggestions:

1) The Li/Li$^+$ electrode potential scale should indicate the solvent and lithium salt concentration, i.e. “E vs. Li/Li$^+$ in 0.1 M $LiClO_{4.}$ in DMSO ” Attention should be paid to the existence of a stable liquid junction potential when using a jacketed reference electrode. The quasi-reversible reference electrodes if used, have to be calibrated always with the ferrocene/ferrocenium couple. This is also true for Na/Na$^+$, K/K$^+$. Mg/Mg^{2+}, etc. scales.
2) Given the high reactivity of lithium metal with organic solvents it is not recommend to use lithium metal directly in contact with lithium ion containing electrolyte as a reference electrode.
3) If the potential scale is referenced to the Li/Li$^+$ scale, always inform the conditions of the Li/Li$^+$ electrode: solvent, salt and its concentration. Also such reference to the Li/Li$^+$ system is only of value if the done in the same solution that was used for the experimental electrolyte. For example, if the experiment was done in DMSO-based solution, the scale should not be calibrated to Li/Li$^+$ measured in the organic carbonates! This is also true for Na/Na$^+$, K/K$^+$. Mg/Mg^{2+}, etc. scales.
4) Ferrocene/ferrocenium as an internal reference redox system recommended by the IUPAC[13] has been used by Laoire and coworkers[16] in 1 M $LiPF_6$ with 1:1 EC:EMC solvent in lithium – ion battery studies since the potential of ferrocene/ferrocenium couple does not vary appreciably with the solvent, and also the potential may be correlated to the aqueous solutions.

However, in lithium-0_2 systems it should not be used as internal potential reference since ferrocene is not stable in the presence of oxygen reduction products as has been shown by Chen and co-workers[17] and in that case it can be used as external standard.

5) We suggest the authors to use an important reference for non-aqueous electrochemistry: "Non-aqueous solvents for electrochemical use" in Eletroanalytical Chemistry series.[18]
6) In the battery community it is often reported the potential of a two-electrode measurement with reference to the Li/Li^+ electrode. We recommend to quote it as the difference between the positive and negative lithium electrode and not 'versus' any specific reference value.

Conclusions

In this perspective we have highlighted the importance of the reference potential scale in different aprotic solvents and the strong dependence of the M/M^{z+} ($M = Li, Na, K, Mg$, etc.) electrode potential on the metal ion solvation energy. For the Li-oxygen battery we have shown the inconsistency in previous reports of the Li/Li^+ scale referred to different solvents.

This flaw in the potential scale can hinder our understanding of complex chemical systems in metal-air batteries. Here we have made suggestions in order to overcome the potential scale ambiguity and encourage practitioners in the field to follow them.

Acknowledgments

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