Electrochemical stability of ether based salt-in-polymer based electrolytes: Computational investigation of the effect of substitution and the type of salt

S. Pandian[a], S.P. Adiga[a,*], P. Tagade[a], K.S. Hariharan[a], K.S. Mayya[a], Y.-G. Lee[b]

[a] Next Generation Research (SAIT-India), Samsung R&D Institute India-Bangalore, #2870 Phoenix Building, Bagmane Constellation Business Park, Outer Ring Road, Doddanekundi Circle, Marathahalli Post, Bangalore 560 037, India
[b] Samsung Advanced Institute of Technology (SAIT), Samsung Electronics Co., Ltd., 130, Samsung-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do, 16678, South Korea

HIGHLIGHTS

- Electrochemical windows of salt-in-polymer electrolytes are investigated.
- Explicit inclusion of salt molecules in the electrochemical window calculations is important.
- Cathodic limit of the electrolyte is defined by reduction potential of the salt anion.
- Perfluoropolyether system shows better electrochemical stability than polyethylene oxide.

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ABSTRACT

The electrochemical stability window (EW) of polyether based salt-in-polymer electrolytes was investigated using density functional theory (DFT) calculations. The electrolyte systems investigated consisted of poly-ethylene oxide (PEO) in either lithium-bis(trifluoromethanesulfonyl)imide (LiTFSI) or lithium-hexafluorophosphate (LiPF$_6$) salt and the EW was determined by performing calculations of reduction and oxidation potentials of isolated ethylene oxide (EO) oligomer and the respective salt species in a continuum solvent. The simulations suggest that the cathodic limit of the polymer-salt system is defined by the reduction potential of the salt anion and that both salt anions considered are unstable against Li anode. The anodic limit is defined by EO and it is stable against most commercial cathodes. Including explicit salt molecules in the calculations shows that the predicted EW is changed by ~0.4 V. The calculations further reveal that the EW is dependent on the type of the salt molecule. Perfluoropolyether, a perfluorinated analog of PEO that has lower reduction potential and higher oxidation potential in isolation as compared to PEO, improved both oxidation and reduction stability of the polymer-salt system. Substitution of other functional groups to PEO improved the electrochemical stability to potentially accommodate higher voltage window requirements.

1. Introduction

In response to the ever growing demand for better Li-ion batteries there are two key strategies that are being pursued to meet the higher energy density needs [1–3]. One strategy is to use high-voltage electrode materials that, for equivalent charge capacity, provide higher energy density. However, high operational voltages also mean that the constituent materials are subjected to harsher electrochemical environment, and hence, demand a wider voltage stability window [4]. A second strategy is to use higher capacity materials such as Li metal anode that promise to deliver as much as ten times the capacity of graphite anodes. To make safe and highly reversible batteries using Li metal anode, however, one of the greatest challenges has been to find

an electrolyte that is stable against Li and that helps prevent lithium dendrite growth that eventually causes internal short circuit. Even though most commercial batteries use liquid electrolytes based on lithium salts containing organic solvents, their limited EW and flammability issues have demanded exploration of safer alternatives such as solid polymer electrolytes (SPE). By far the most investigated polymer electrolyte is poly-(ethylene) oxide (PEO) or composites thereof due to their excellent stability and non-flammability, although they exhibit ionic conductivities an order of magnitude lower than liquid organic electrolytes [5–8]. Naturally, previous studies of PEO based electrolytes have mostly focused on ionic conductivities and Li$^+$ transference numbers and how to improve them [9,10] and very little attention has been focused on electrochemical stability window of PEO or other solid

polymer electrolytes. As the quest for high voltage electrode materials and long and safe battery cycling continues, developing SPEs with wide EWs, in particular, stability against lithium becomes important.

The EW of the electrolyte determines the safe operational voltage window outside of which the electrolyte will degrade. The EW is set by the oxidation and the reduction potentials of the electrolyte and is related to energy levels corresponding to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively [11,12]. If a passivating, kinetic barrier between the electrode and the electrolyte is not formed, then anode potentials above the LUMO of the electrolyte will tend to reduce the electrolyte and cathode potentials below the HOMO of the electrolyte will tend to oxidize the electrolyte. For example, in the case of Li metal anode, which is very electropositive (-3.04 V redox-potential vs. SHE, which lies above the LUMO of most organic molecules), there is a high tendency for electrolyte species exposed to it to get reduced. While initial decomposition of the electrolyte and the subsequent formation of a protective solid-electrolyte interphase (SEI) is desired for the stabilization of Li anodes, the repeated stripping and plating of Li atoms beneath the SEI upon electrochemical cycling is bound to initiate cracks in the SEI. This will lead to exposure of new (unreacted) electrolyte to metallic Li, leading to progressive electrolyte decomposition [13]. Therefore it is important to choose the electrolytes such that the anode and cathode potentials lie within the electrochemical window of the electrolyte.

In the recent past, density functional theory (DFT) calculations have been used to investigate EW of electrolytes and have also been employed to down-select and design stable electrolytes [11,12,14]. To the best of our knowledge, these calculations have focused on liquid electrolytes based on organic and ionic liquid based electrolytes and there has not been any investigation on the EW of polymer based electrolytes. In this work we systematically investigate the EW of ether based salt-in-polymer electrolytes. A majority of EW calculations in the literature rely on determination of redox potentials using first-principles electrochemical calculations on candidate molecules in implicit or explicit solvents, without necessarily considering the specific chemical environment which the electrolytes are exposed to in a real battery. While there is a rich chemical environment that the electrolyte is exposed to, the most dynamic of these is presented by variation in salt concentration presented by concentration gradients developed during charging and discharging. The interactions with ions are typically omitted in screening studies, while they are likely to alter the redox potentials of the electrolyte components. Here, we investigate the effect of salt type on the stability of poly-(ethylene oxide) based electrolytes by explicitly including them in the calculations. Further, we explore how functionalizing PEO chains with electron withdrawing and electron donating groups can help widen the EW. This strategy has not been systematically studied, which motivates the present work.

The presented computational results indicate that the reduction and oxidation potentials of PEO based salt-in-polymer electrolytes are determined by salt and PEO molecules, respectively. The oxidation potential can be improved by using substitutional groups to PEO on the backbone or the sidechain. To improve the reduction stability, use of more stable salts is needed. We believe these results should be useful to inform future experimental efforts towards design of stable salt-in-polymer electrolytes for use with Li metal anodes.

2. Computational details

Quantum chemical calculations were performed using the Gaussian 09 software package [15]. The B3LYP functional and 6-311 + G (d,p) basis sets were employed with the polarized continuum model [16] to describe the solvation environment. The solution environment was constructed using an effective dielectric constant of 78.35 corresponding to that of water. The geometries of all charged and neutral molecules were optimized in the solvation environment without any

constraints. Frequency calculations were carried out to check for minima on the potential energy surface. The oxidation potential (E_{ox}) was calculated as the difference in the total free energies of the oxidized and neutral molecules, where the oxidation reaction involves removing an electron from the neutral molecule. The reduction potential (E_{red}) was calculated as the negative of difference in the total free energies of the reduced and neutral molecules, where the reduction reaction involves adding an electron to the neutral molecule. All oxidation and reduction potentials were referenced to the Li/Li$^+$ potential [17] by subtracting the value by 1.39 V, allowing us to omit 'vs. Li/Li$^+$' hereon. The range of voltages between the reduction and oxidation potentials define the EW. The stability criterion followed in the paper is as follows: a lower reduction potential (more negative) implies higher stability towards reduction and higher oxidation potential (more positive) implies higher stability towards oxidation.

In addition to the redox potentials, the HOMO and LUMO energies of the molecule were noted to understand their correlation with the calculated redox potentials. The solution phase eigenvalues at the same level of theory for HOMO and LUMO are considered. In literature, the relation between HOMO and oxidation stability and LUMO and reduction stability have previously been explored in screening potential battery electrolyte materials [18] and organic additives [19]. Though the correlation holds good for individual components (anion or functional derivatives of additives), differences can arise when two or more components are considered for an electrolyte (eg. including Li salt).

3. Results and discussion

Before we present a detailed discussion of our results, it is important to note that a direct comparison of DFT calculated EW with experimentally measured EW is not very straight forward. This is because the experimentally measured electrochemical window depends heavily on the measurement conditions. Typically, the electrochemical window is determined by performing cyclic voltammetry and measuring the cathodic and/or anodic currents, corresponding to electrolyte reduction or oxidation. However, reported EWs in the literature differ widely in the experimental conditions, as they depend on the type of electrodes, the current cut-off used to determine the beginning of redox reactions and the references used. Additionally, the stability window of an electrolyte in a real working electrochemical cell is affected by the exposure to complex, spatially and temporally varying chemical environment present in the cell, the effects of which are difficult to incorporate in first principles calculations. The absolute electrochemical stability window of an electrolyte in an electrochemical cell is highly dependent on the local thermochemical environment under operational conditions. Thus, the calculated electrochemical windows are useful in making comparisons between different electrolytes and the relative effect of various constituents on the EW.

3.1. The effect of number of EO units on redox potentials

In our calculations we used oligomers of EO to estimate the electrochemical window of PEO, since performing DFT calculations on long PEO chains becomes computationally prohibitive. Therefore we first performed an analysis of the effect of number of EO units on the redox potentials and the EW.

Fig. 1 summarizes the calculated electrochemical windows (Fig. 1(a)) and the frontier orbital energy levels of oligomers of EO (Fig. 1 (b)) with the number of EO units (n) varying from 1 to 10. The minimum of the stable potential region is the cathodic limit (where reduction of PEO is expected to occur or E_{red}), while the maximum is the anodic limit (where oxidation of PEO is expected to occur or E_{ox}). The EW values for each oligomer calculated as the difference between E_{ox} and E_{red} is given in Fig. 1(a). We focus mainly on the EW rather than the maxima or minima in this case, as we analyze the effect of varying monomer units on the stability window of PEO and to choose a