Electrochemical Reaction Analysis Using Density Functional Calculation + Implicit Solvation Model

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We have studied charge transfer reaction at electrode/electrolyte solution interfaces in Li-ion batteries (LIB) using density functional theory (DFT) calculation combined with implicit solvation model. This simulation is called ESM-RISM,[1] i.e., the effective screening medium (ESM)[2] + the reference interaction site model (RISM)[3], and implemented in Quantum Espresso package.[4]

This year, we focused on Li-ion transfer reaction (*R*) at the interface of graphite electrode/solid electrolyte interphase (SEI)/ solution (1 M $LiPF_6$ EC) as follows:

$$Li_nC_{6m}H_l + hLi_2CO_3 \rightarrow Li_{n-1}C_{6m}H_l + hLi_2CO_3 + Li^+(1\text{ M }LiPF_6\text{ EC}) \quad (R).$$

ESM-RISM calculations were performed on the configuration of a vacuum/slab/soltion system as shown in Fig. 1 (a), where the DFT slab domain represents Li-inserted graphite ($Li_nC_{6m}H_l$)/SEI (inorganic lithium carbonic acid, hLi_2CO_3), and the RISM solvent and ions, (EC, Li^+, and PF_6^-). Since the electrolyte concentration of typically 1.0 M gives a small Debye screening length of several angstroms, the RISM region (> 40 Å) used in this calculation was sufficiently long.

Figure 1 (b) shows the grand potential Ω of pristine, $Li_nC_{6m}H_l/hLi_2CO_3$, and V_{Li} + Li^+, $Li_{n-1}C_{6m}H_l/hLi_2CO_3$ + Li^+(1 M $LiPF_6$ EC), as a function of the chemical potential of an electron μ_e. In the ESM-RISM calculations, μ_e is measured from the potential at inner solution region Φ_S. It is possible to compare μ_e at different electrodes contacting the same solution directly.[5] The difference between two equilibrium potentials on different electrodes provides the electromotive force, E_{emf}, between the two electrodes as:

$$E_{emf} = -(\mu_{eq} - \mu_{Li/Li^+})/e \quad (1),$$

where μ_{eq} represent the equilibrium potential of reaction (*R*) and *e* is the elementary charge. Once an equilibrium potential μ_{Li/Li^+} of Li transfer reaction at Li metal electrode is determined in the ESM-RISM calculation, the electromotive force (or electrode potential relative to the Li/Li^+ reference) can be immediately derived. Because it was obtained $\mu_{Li/Li^+} = -3.06$ eV vs Φ_S in a previous study,[6] the result of $\mu_{eq} = -3.17$ eV vs Φ_S gave E_{emf} = 0.11 V vs Li/Li^+, which is in good agreement with experiment (0.1 – 0.2 V vs Li/Li^+).

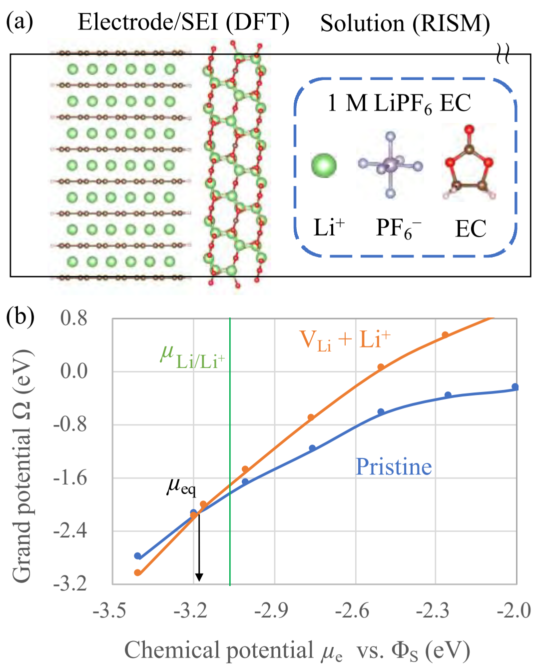

Fig. 1: (a) ESM-RISM configurations of the vacuum/slab/solvent system: the simulation cells of $Li_nC_{6m}H_l/hLi_2CO_3$|1M $LiPF_6$ EC interfaces. (b) Profiles of Ω as a function of μ_e. The blue and orange lines show Ω of $Li_nC_{6m}H_l/hLi_2CO_3$ and $Li_{n-1}C_{6m}H_l/hLi_2CO_3$ + Li^+(1 M $LiPF_6$ EC), respectively.

Additionally, it was confirmed that the equilibrium potential of reaction (*R*) cannot depend on such as the thickness and component of SEI. In the next physical year, the activation energy of reaction (*R*) will be revealed under operated LIB working conditions.

References

[1] S. Nishihara and M. Otani: Phys. Rev. B **96** (2017) 115429.

[2] M. Otani and O. Sugino: Phys. Rev. B **73** (2006) 115407.

[3] A. Kovalenko and F. Hirata: J. Chem. Phys. **110** (1999) 10095 (1999).

[4] P. Giannozzi et al.: J. Phys.: Condens. Matter **21** (2009) 395502; **29**, (2017) 465901.

[5] J. Haruyama, T. Ikeshoji, and M. Otani, Phys. Rev. Mater. **2** (2018) 095801.

[6] J. Haruyama, T. Ikeshoji, and M. Otani: J. Phys. Chem. C **122** (2018) 9804.