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Electrochemical potential window of battery electrolytes: the HOMO–LUMO misconception†

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A widespread misconception in the lithium ion battery literature is the equality of the energy difference of HOMO and LUMO of the solvent with the electrochemical stability window. HOMO and LUMO are concepts derived from approximated electronic structure theory while investigating electronic properties of isolated molecules, and their energy levels do not indicate species participating in redox reactions. On the other hand, redox potentials are directly related to the Gibbs free energy difference of the reactants and products. While redox potentials in some cases show strong correlation with HOMO energies, the offset can be of several eVs. Presence of electrolytes and other molecules can also significantly affect the redox potentials of the solvent leading to offset as high as 4 eV from the HOMO energies. In this opinion we provide a correct thermodynamic representation for the electrochemical stability of the electrolyte, based on redox potentials and Fermi level of the electron in solution, and demonstrate that the use of terms HOMO and LUMO should be avoided when talking about the electrochemical stability of electrolytes. Instead, it is more correct to speak of potential of electrolyte reduction at negative potentials, and of potential of solvent oxidation at positive potentials.

Broader context

The stability window of a battery electrolyte is widely believed to be represented with the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the solvent molecules. This misconception leads to significant misinterpretations regarding electrolyte stabilities, and can lead to wasted efforts utilizing solvents that appear to be stable in terms of HOMO and LUMO energies, but are in fact instable in terms of oxidation and reduction potentials. Electrolyte stability is much more complex issue, requiring considering the redox potentials of the solvent, but even further, the reactions with the other solvent molecules and electrolyte salts, and even the surfaces of the electrode materials. Hence, we recommend abandoning the utilization of HOMO and LUMO when describing the electrolyte stability.

Many battery reports incorrectly use the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the solvent to signify the redox potentials where either the solvent or the electrolyte oxidation/reduction take place.[1–10] For example, Fig. 1 taken from the review of Goodenough *et al.*[4] in this journal, and appearing in many courses on battery research, claims that the stability of the electrolyte solvent is defined by the energy levels of the HOMO and LUMO of the electrolyte, *i.e.* at electron energies higher than LUMO the solvent/electrolyte is reduced and at electron energy levels lower than HOMO the solvent/electrolyte is oxidized. HOMO and LUMO are concepts derived from approximated electronic structure theory while investigating electronic properties of isolated molecules, and their energy levels do not indicate species participating in redox reactions. On the other hand, redox potentials are directly related to the

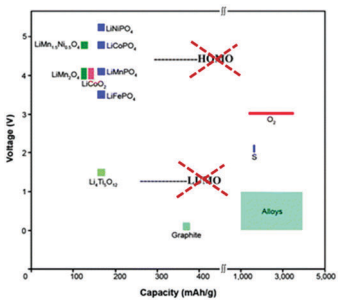

Fig. 1 Example of a misuse of the concepts of HOMO and LUMO for lithium-ion battery literature. Modified with permission from ref. 4.

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Gibbs free energy difference of the reactants and products. The purpose of this opinion is to show that this incorrect use of HOMO and LUMO as an indication of the electrochemical stability window of the solvent violates the principle of electrochemistry and gives an erroneous representation.

To illustrate that HOMO and LUMO have very little to do with the oxidation and reduction potentials of the solvent let us consider the case of water. From an electronic structure perspective, liquid water is an oxide with a band gap of 8.7 eV to 8.9 eV.[11,12] If the HOMO–LUMO energy difference would reflect the electrochemical potential window, water should be a solvent of choice for Na-ion batteries. Unfortunately, the thermodynamic potential window of water is only 1.23 V[13] limited by the hydrogen evolution at −4.02 eV and oxygen evolution at −5.25 eV, both at pH 7[13] (assuming the IUPAC recommendation of 0 V *vs.* standard hydrogen electrode (SHE) corresponding to the energy level of −4.44 eV on the absolute scale where the energy of electron in vacuum is 0 eV[14]). The different energy levels are illustrated in Fig. 2 clearly showing the lack of relation between the HOMO–LUMO energy gap for water and the Fermi levels for the electron in solution for the reduction and oxidation of water.

At this point, it is important to recall the concept of Fermi level for the electron in solution for a given redox couple (Ox/Red).[15,16] The electrochemical potential of an electron in a solution containing a redox couple can be defined with the virtual redox reaction $Ox^S + e^{-,S} \rightleftharpoons Red^S$. At equilibrium the electrochemical potential for the virtual electron in solution is defined as the difference between the electrochemical potentials of the reduced and oxidised species, respectively, and it is equivalent to the energy required to bring an electron from vacuum to a solution containing a redox couple.[17]

$$\tilde{\mu}^S_{e^-} = \tilde{\mu}^S_{Ox} - \tilde{\mu}^S_{Red} = \mu^S_{e^-} - e\phi^S = \alpha^S_{e^-} - e\psi^S \qquad (1)$$

where α is the real chemical potential, $\phi^S = \chi^S + \psi^S$ is the Galvani potential (also called the inner potential) of the solution phase, where χ^S is the surface potential (associated with the interfacial dipole of the solution–vacuum interface) and ψ^S is the outer potential of the solution phase (associated with the excess charge of the solution). The real chemical potential includes the contribution from the surface potential.

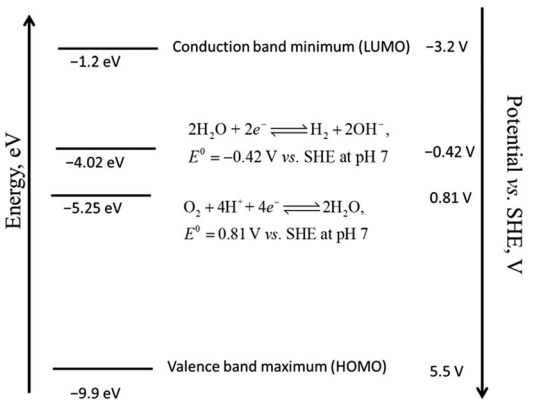

Fig. 2 HOMO, LUMO and the thermodynamic potential window of the stability of water at pH 7.

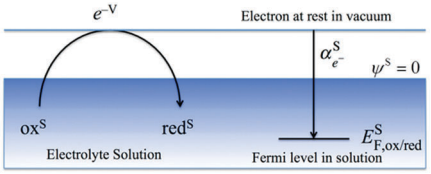

Fig. 3 Concept of the Fermi level of an electron in solution for a given redox couple.

We can define the standard redox potential on the absolute vacuum scale (AVS) by considering the virtual redox reaction between an oxidized species in solution and an electron at rest in vacuum: $Ox^S + e^{-,V} \rightleftharpoons Red^S$ and by utilizing the definition of the AVS scale that $\tilde{\mu}^V_{e^-} = 0$:

$$-\Delta G_{reduction} = \tilde{\mu}^S_{Ox} - \tilde{\mu}^S_{Red} = e[E_{Ox/Red} + \phi^S]^S_{AVS} \qquad (2)$$

Now the electrochemical potential of an electron in solution can be defined by comparing eqn (1) and (2):

$$-\tilde{\mu}^S_{e^-} = e\left[E_{Ox/Red} + \phi^S\right]^S_{AVS} \qquad (3)$$

As shown in Fig. 3, if the solution phase does not carry any excess charge, $\psi^S = 0$ and

$$-\alpha^S_{e^-} = e\left[E_{Ox/Red} + \phi^S\right]^S_{AVS,\psi^S=0} = \alpha^S_{Ox} - \alpha^S_{Red} \qquad (4)$$

This standard redox potential on the AVS scale can be obtained by a thermodynamic cycle considering the solvation energies of Ox and Red, and the ionization energy in vacuum of Red, as illustrated for the Fe(III)/Fe(II) couple in the ESI.†

$$[E^0_{Ox/Red}]^W_{abs} = \Delta G^{\ominus}_{Oxidation}/nF = -(\Delta G^{\ominus}_{hyd,Red} - E_{I,Red} - \Delta G^{\ominus}_{hyd,Ox})/nF \qquad (5)$$

where $\Delta G^{\ominus}_{hyd}$ is the work to solvate the ion and E_I is the ionization energy in vacuum.

On the other hand, the Fermi level of the electron in solution, $E_{F\,Ox/Red}$ (eV) is related with the standard redox potential in the standard hydrogen electrode scale (SHE), $E^0_{Ox/Red}$ (V) by[18]

$$E^S_{F,Ox/Red} = -e\left(\left[E^{\ominus}_{Ox/Red}\right]^S_{SHE} + \frac{kT}{ne}\ln\left(\frac{a^S_{Ox}}{a^S_{Red}}\right) + \phi^S + \left[E^{\ominus}_{H^+/\frac{1}{2}H_2}\right]^W_{AVS}\right) \qquad (6)$$

where $\left[E^{\ominus}_{H^+/\frac{1}{2}H_2}\right]^W_{AVS} = 4.44$ V is the potential of the standard hydrogen electrode (SHE) on the absolute vacuum scale (AVS),[14] k is the Boltzmann constant, T is temperature, e is the elementary charge, a_i is the activity of the species i (defined as $a_i = \gamma_i c_i/c^0$ where γ_i is the activity coefficient, c_i is the concentration of species i and c^0 is the standard concentration 1 mol L^{-1}) n is the number of electrons transferred in the redox reaction $Ox + ne^- \rightarrow Red$.

Indeed, in Fig. 1 it is important to compare the Fermi levels for the electron in the electrode with the Fermi levels for the electron in solution for the two redox couples limiting the stability of the electrolyte. In the case of pure water, the redox couple for the reduction is H_2O/H_2 and that for oxidation O_2/H_2O.

Another interesting example is the Fe(III)/Fe(II) couple in aqueous solution. The hexa-aqua complexes of Fe^{2+} and Fe^{3+} show lowest excitation energies of 1.02 eV and 1.56 eV corresponding to different d–d transitions as determined experimentally[19,20] and by DFT calculations.[21] Hence, these complexes show HOMO–LUMO gaps of 1.02 eV and 1.56 eV (in truth these are not actually HOMO–LUMO transitions, but transitions between one filled or partially filled t_g or e_g orbital and the other partially filled t_g or e_g orbital at a higher energy[21]). Vertical ionization energies (corresponding to the energy of HOMO) of these complexes have been determined experimentally as 7.1 and 10.3 eV.[22,23] On the other hand, the electrochemical potential of an electron can be calculated as −5.21 eV (as illustrated in the ESI,† or by using the standard potential of 0.77 V *vs.* SHE[13] and the hydrogen potential of −4.44 V on the absolute vacuum scale[14] and not considering the effect of ϕ^S). The energy levels are summarized in Fig. 4. The difference of these two energies is due to the reorganization of the complex with its solvation shell, *i.e.* sudden removal of electron from Fe(II) complex leaves the resulting Fe(III) complex in an unoptimized configuration, and relaxation to typical Fe(III) configuration results in a reorganization energy of 1.92 eV.[19]

Hence, $[Fe(H_2O)_6]^{2+}$ has a HOMO at −7.1 eV and a LUMO at −6.1 eV, while the corresponding values for $[Fe(H_2O)_6]^{3+}$ are −10.3 eV and −8.74 eV, and the standard redox potential of $[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ couple is −5.21 eV (or 0.77 V *vs.* SHE). Additionally, the standard redox potential of the $[Fe(H_2O)_6]^{2+}/Fe$ couple (*i.e.* electrodeposition of iron) is −3.99 eV (or −0.447 V *vs.* SHE[13]). It is clear that there is no clear connection between HOMO and LUMO energies and redox potentials for these redox couples. Another effect worth to note is that the redox potential (and also the Fermi level of electrons in the redox pair) depends on the concentration ratio of redox active species,[16] while HOMO and LUMO energies are independent of concentrations. For example, a solution containing 10 : 1 ratio of Fe(II) to Fe(III) has 59 mV lower redox potential, as indicated by Nernst equation. For 100 : 1 ratio the shift is 118 mV from the standard potential. In terms of Fermi level, it is easier to bring an electron into a system with higher ratio of Fe(II) to Fe(III). As a side note, curiously the experimental vertical ionization energies of aqueous Fe(II) and Fe(III) ions are much smaller than reported for atomic ions (30.7 and 54.8 eV for Fe(II) and Fe(III), respectively[24]). This difference of a factor of 5 is most likely due to the dipole-ion interactions stabilizing the solvated ion. In fact, solvation energies of Fe(II) and Fe(III) are 20 and 45 eV, respectively.[17]

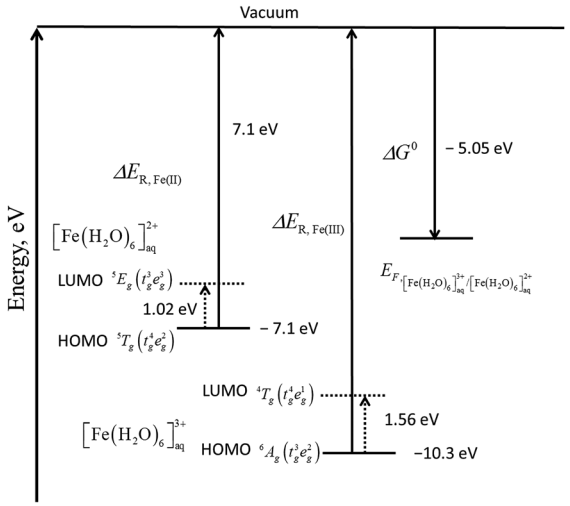

Fig. 4 Energy levels of different aqueous Fe-species, and the Fermi level of electrons in Fe(III)/Fe(II) redox couple.

On the other hand, many redox couples in non-aqueous solvents show a linear empirical correlation between the HOMO and LUMO energies and the redox potentials. For example, calculated LUMO energies of 74 organic redox active compounds with different functional groups showed a linear relationship with experimental reduction potentials with a slope of −1.12, intercept of −4.34 and R^2 of 0.9917.[25] However, this correlation is by no means universal, as different studies with a set of different molecules show slopes of −1.4 *etc.*[26] For example, the correlation of the experimental ionization energies[23] (HOMO) and tabulated standard potentials[13] of aqueous transition metal complexes included in the Fig. S2 in ESI,† show rather poor correlation with a slope of −1.23, intercept of −8.9 eV and R^2 of 0.32 for reduction and slightly better correlation for oxidation with the slope of −1.09, intercept of −7.3 eV and R^2 of 0.71.

Finally, the HOMO energies of common battery solvents have been calculated as −10.51 eV and −9.64 eV for ethylene carbonate and dimethylcarbonate, while the calculated oxidation potentials are 7.87 V and 7.07 V *vs.* absolute vacuum scale, or −7.87 eV and −7.07 eV on the energy scale.[27] So in fact, utilization of the HOMO energy to indicate if the electrolyte would be stable would lead to overestimated electrolyte stability. Additionally, H- and F-transfer reactions should be considered to accurately calculate the onset potentials for electrolyte decomposition.[28] For example, direct oxidation of ethylene carbonate (potential of 7.87 V[27]) does not take place during battery operation. However, ethylene carbonate complex with PF_6^- anion is oxidized at lower potentials while forming HF, and H-transfer to another EC coupled with oxidation decreased the computational oxidation potential further to 6.4–6.6 V on the AVS scale (5–5.2 V *vs.* Li^+/Li). The oxidation can proceed by different paths, producing CO_2 and ethanol radical cation after multiple steps.[29] Hence, the oxidation of isolated ethylene carbonate occurs at almost 2 V higher potentials, and the HOMO energy is 4 eV lower than the energy levels where the oxidation of the solvent actually occurs.

These examples illustrate that the use of terms HOMO and LUMO should be avoided when talking about the electrochemical stability of electrolytes. Instead, it is more correct to speak of potential of electrolyte reduction at negative potentials, and of potential of electrolyte oxidation at positive potentials, as shown in Fig. 5. This distinction seems to be clear for

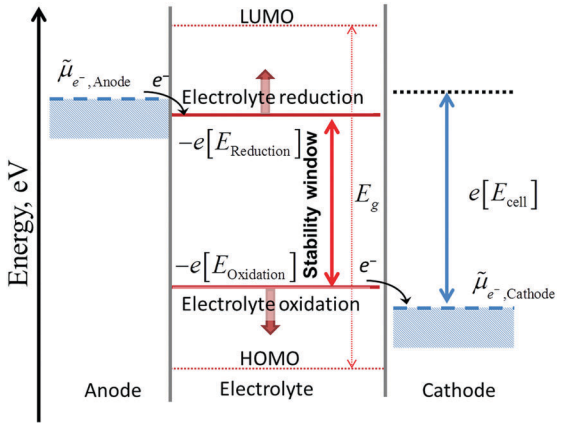

Fig. 5 Correct notation for the negative and positive potential limits for the electrolyte stability, and the energy levels of HOMO and LUMO.

researchers doing the calculations,[28] but not so clear for the experimentalists.[1–10]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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