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Electronic Supplementary Information

Electrochemical potential window of battery electrolytes: the HOMO-LUMO misconception

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1. Thermodynamic cycle to estimate the absolute redox potential of Fe(III)/(II) couple

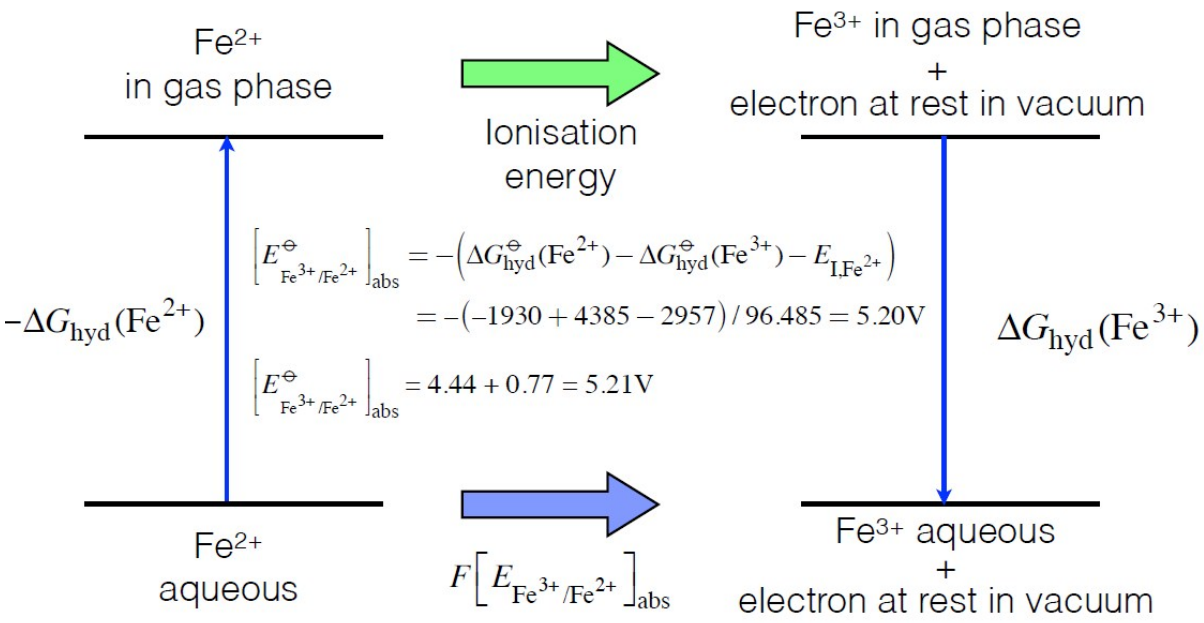

Figure S1. Thermodynamic cycle to estimate the absolute redox potential of Fe(III)/(II) couple considering the work to remove the solvation shell upon transfer of the Fe^{2+} into the gas phase, ionization energy and the solvation energy of Fe^{3+}, resulting in the absolute potential of 5.20 V.[1] The alternative approach is to utilize the standard redox potential of Fe(III)/(II) couple of 0.77 V *vs*. SHE and the definition of the SHE at the absolute vacuum scale of 4.44 V, resulting in the absolute potential of 5.21 V.

2. The correlation of the experimental ionization energies (HOMO) and tabulated standard reduction potentials of aqueous transition metal

Table S1.Experimental vertical ionization energies (VIE) of some hexaqua complexes of transition metal ions[2,3] and the corresponding standard oxidation and reduction potentials.[4]

Species	VIE, eV	Redox pair	E_{red}, V	Redox pair	E_{ox}, V
Ti^{3+}	7.05	Ti(III)/(II)	–0.369		
V^{3+}	8.41	V(III)/(II)	–0.255	V^{3+}/VO^{2+}	0.337
Cr^{3+}	9.48	Cr(III)/(II)	–0.407	Cr^{3+}/CrO_2	1.48
Cr^{2+}	6.76	Cr(II)/(0)	–0.913	Cr^{3+}/Cr^{2+}	0
Mn^{2+}	8.82	Mn(II)/(0)	–1.185	Mn^{3+}/Mn^{2+}	1.5415
Fe^{3+}	10.28	Fe(III)/(II)	0.771	$HFeO_4^-/Fe^{3+}$	2.07
Fe^{2+}	7.13	Fe(II)/(0)	–0.447	Fe^{3+}/Fe^{2+}	0
Co^{2+}	8.7	Co(II)/(0)	0.28	Co^{3+}/Co^{2+}	1.92
Ni^{2+}	9.45	Ni(II)/(0)	–0.252	NiO_2/Ni^{2+}	1.678
Cu^{2+}	9.65	Cu(II)/(I)	0.153	Cu^{3+}/Cu^{2+}	2.4

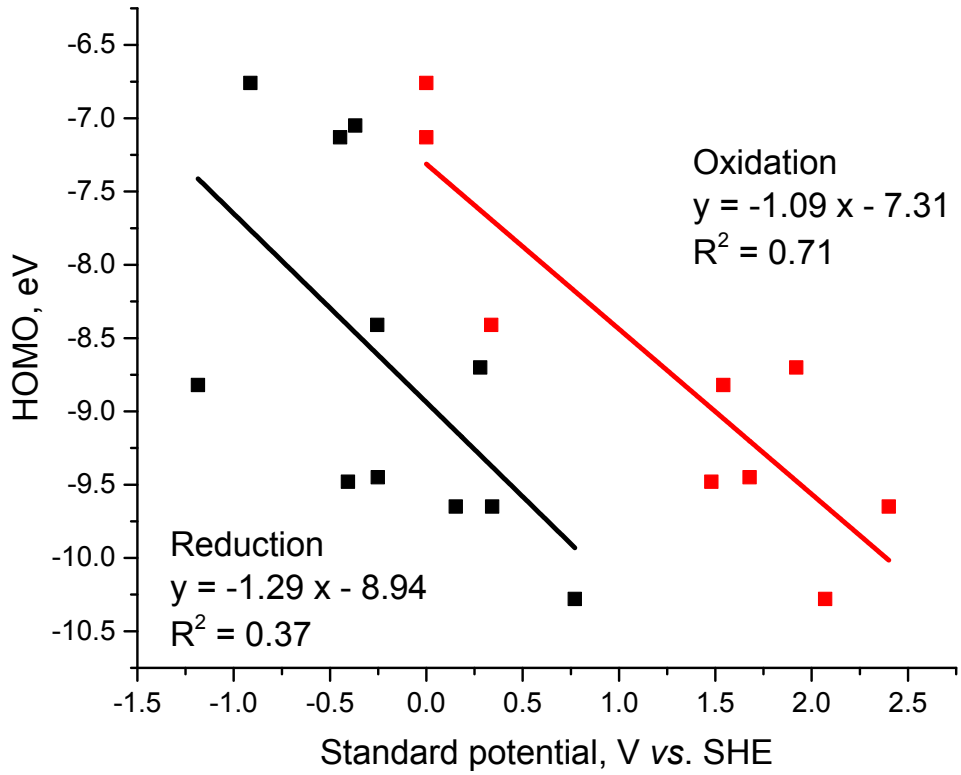

Figure S2. Correlation of the experimental HOMO energies (vertical ionization energy) and standard reduction potentials (black) and oxidation potentials (red) of the transition metals.

3. References

1 H. H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press, Lausanne, 2004.

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4 P. Vanýsek, in *CRC Handbook of Chemistry and Physics*, eds. W. M. Haynes, T. J. Bruno and D. R. Lide, Taylor and Francis Group, LLC, 96th edn., 2016, p. 5:79-88.