

Supplementary information

Reduction energy for the THF solvent

We provide DFT calculation of the dependence of the reduction potential on the dielectric permittivity of the Mg^{2+} ion solvated by the tetrahydrofuran (THF) molecules. Coordination number in such system is $CN = 6$ ¹. Results of the simulation are presented in the figure 1. A significant dependence of the reduction potential on the dielectric permittivity is also observed for the $Mg^{2+}THF_6$. The dependence is slightly weaker due to larger size of the solvation shell of $Mg^{2+}(THF)_6$ complex compared with $Mg^{2+}(S2)_3$ complex.

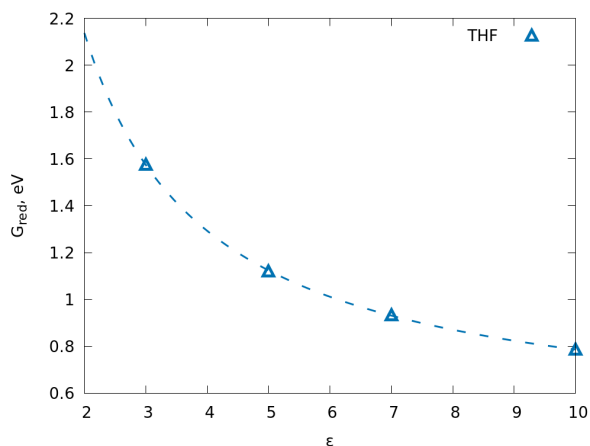


Figure 1 Dependence of the DFT calculated reduction potential (G_{red}) on the dielectric permittivity of the liquid, that surrounds the solvation shell. Mg^{2+} ion is solvated by 6 THF molecules.

Effect of the ion electric field on ϵ_{op}

Field of the reduced Mg^{1+} ion polarizes the environment around the shell and changes optical properties of the liquid around the shell. Variation of the optical properties under the applied electric field is caused by the electro optic Kerr effect^{2,3}.

Amplitude of the electric field near the reduced Mg^{1+} ion may be estimated as.

$$E = \frac{1}{4\pi\epsilon_0} \frac{e}{R^2}, \quad (1)$$

where $R \approx 4 \text{ \AA}$ is the distance from the ion to the molecules outside the solvation shell. Calculation of E using the relation (1) provides $E = 5.7 \times 10^9 \text{ V/m}$.

Amplitude of the Kerr effect on the optical permittivity of the liquid may be estimated as³

$$\Delta n = \lambda B E^2, \quad (2)$$

where Δn is a change of the refractive index, B is the Kerr constant, E is the electric field and λ is the wavelength of the light used to measure the Kerr constant.

The value of the Kerr constant for the M4 and S2 solvents is unknown. However, it may be approximated from the values for water³ $2.96 \times 10^{-14} \text{ V}^{-2}\text{m}$. This value is determined for $\lambda = 633 \text{ nm}$.

Estimation of the amplitude of the Kerr effect using E from the relation (1) and Kerr constant for water results in $\Delta n = 0.608$. This corresponds to change in ϵ_{op} from 1.95 to 3.95. This closely resembles the value of the optical permittivity used in this work ($\epsilon_{op} = 3.65$).

Such effect does not appear in case of the single ion reduction. There is no electric field around reduced monovalent ion such as in the reaction $Li^+ + e = Li^0$. Thus, an experimental value of the optical permittivity may be used for such reaction. However, there is an electric field around the reduced divalent magnesium ion $Mg^{2+} + e = Mg^+$. Thus, Kerr effect on the optical properties of the liquid around the reduced divalent ions should be taken into account.

Derivation of the ion-surface effect

An effect the electrode surface may be derived from the integration of the electric field energy around the solvated ion near the electrode surface. This derivation results in 1/4 and 3/4 factors for the effect of interaction with electrode and with solvent. The derivation closely resembles derivation of the Born model.

The following equations are used

$$G = G(\text{vacuum}) - G(\text{solution}), \quad (3)$$

where $G(\text{vacuum}) = \frac{q^2}{32\pi\epsilon_0 R_{shell}}$ is the energy of the electric field of the ion in vacuum, that does not depend on the dielectric permittivity of the solution and $G(\text{solution})$ is the energy of the ion in solution

$$G(\text{solution}) = \frac{1}{2} \epsilon_0 \int \epsilon E^2 dV. \quad (4)$$

Calculation for the electric field of a point charge $E = \frac{q}{4\pi\epsilon_0\epsilon r^2}$ results in

$$G(\text{solution}) = \frac{1}{2} \epsilon_0 \int \epsilon E^2 dV = \frac{1}{2} \epsilon_0 \int \frac{\epsilon q^2}{16\pi^2 \epsilon_0^2 \epsilon^2 r^4} dV = \int \frac{q^2}{32\pi^2 \epsilon_0 \epsilon r^4} dV. \quad (5)$$

Integration of the relation (5) in a system with constant dielectric permittivity leads to the Born model. We are integrating this equation for a space filled with material with dielectric permittivity $\epsilon = \epsilon_1$ and $\epsilon = \epsilon_2$ as presented in the figure 2. It is assumed that solvation shell touches the surface of the electrode. This determines the geometry of the system.

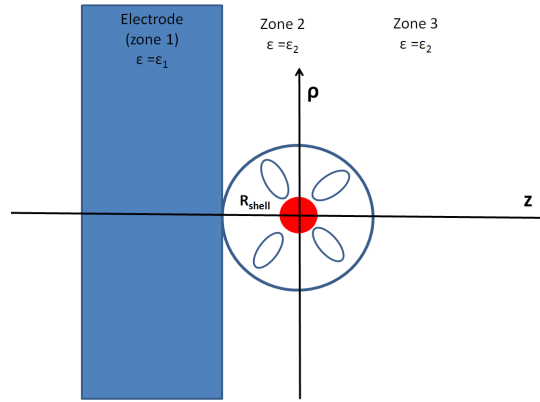


Figure 2 Ion with solvation shell near the electrode surface. ρ and z axes of the cylindrical coordinate system are shown. Integral over the zone 1 is equal to the 1/4 of the total integral.

Spherical symmetry does not appear in the system with electrode. A system with electrode has cylindrical symmetry with z axis perpendicular to the electrode surface. Thus, we use cylindrical coordinates for the integration. As a consequence we use following variables

$$dV = \rho d\rho d\phi dz d\phi \quad (6)$$

$$r^2 = \rho^2 + z^2 \quad (7)$$

Equation, (5) is rewritten as

$$\int \frac{q^2}{32\pi^2 \epsilon_0 \epsilon r^4} dV = \int \frac{q^2}{32\pi^2 \epsilon_0 \epsilon (\rho^2 + z^2)^2} \rho d\rho d\phi dz. \quad (8)$$

Integration over the angle ϕ leads to the simple multiplication of the result by 2π

$$\int_z \int_\rho \int_\phi \frac{q^2}{32\pi^2 \epsilon_0 \epsilon (\rho^2 + z^2)^2} \rho d\rho d\phi dz = \int_z \int_\rho \frac{q^2}{16\pi \epsilon_0 \epsilon (\rho^2 + z^2)^2} \rho d\rho dz. \quad (9)$$

Then we integrate over ρ using $\rho d\rho = 1/2 d\rho^2$

$$\int_z \int_\rho \frac{q^2}{16\pi \epsilon_0 \epsilon (\rho^2 + z^2)^2} \rho d\rho dz = \int_z \int_\rho \frac{q^2}{32\pi \epsilon_0 \epsilon} \frac{d\rho^2 dz}{(\rho^2 + z^2)^2} = \int_z \frac{q^2}{32\pi \epsilon_0 \epsilon} \left(-\frac{dz}{\rho^2 + z^2} \right) \Big|_\rho. \quad (10)$$

We separate integral into three zones (figure 2). Zone 1 is electrode with dielectric permittivity ϵ_1 . It corresponds to $z > 0$ and $\rho < -R_{shell}$. Zone 2 is electrolyte solution above and below the solvation shell with dielectric permittivity ϵ_2 . It corresponds to $-R_{shell} < z < R_{shell}$ and $\rho^2 > R_{shell}^2 - z^2$. Zone 3 is electrolyte solution on the right of the solvation shell with dielectric permittivity ϵ_2 . It corresponds to $z > R_{shell}$ and $\rho > 0$.

$$\int_z \frac{q^2}{32\pi\epsilon_0\epsilon} \left(-\frac{dz}{\rho^2+z^2} \right) \Big|_{\rho} = \int_{z=-\infty}^{z=-R_{shell}} \frac{q^2}{32\pi\epsilon_0\epsilon_1} \left(-\frac{dz}{\rho^2+z^2} \right) \Big|_{\rho=0}^{\rho=+\infty} + \int_{z=-R_{shell}}^{z=R_{shell}} \frac{q^2}{32\pi\epsilon_0\epsilon_2} \left(-\frac{dz}{\rho^2+z^2} \right) \Big|_{\rho^2=R_{shell}^2-z^2}^{\rho=+\infty} + \int_{z=R_{shell}}^{z=+\infty} \frac{q^2}{32\pi\epsilon_0\epsilon_2} \left(-\frac{dz}{\rho^2+z^2} \right) \Big|_{\rho=0}^{\rho=+\infty} \quad (11)$$

First term of the equation (11) is

$$\int_{z=-\infty}^{z=-R_{shell}} \frac{q^2}{32\pi\epsilon_0\epsilon_1} \left(-\frac{dz}{\rho^2+z^2} \right) \Big|_{\rho=0}^{\rho=+\infty} = \int_{z=-\infty}^{z=-R_{shell}} \frac{q^2}{32\pi\epsilon_0\epsilon_1} \frac{dz}{z^2} = \frac{q^2}{32\pi\epsilon_0\epsilon_1} \left(-\frac{1}{z} \right) \Big|_{z=-\infty}^{z=-R_{shell}} = \frac{q^2}{32\pi\epsilon_0\epsilon_1} \frac{1}{R_{shell}} \quad (12)$$

Second term of the equation (11) is

$$\int_{z=-R_{shell}}^{z=R_{shell}} \frac{q^2}{32\pi\epsilon_0\epsilon_2} \left(-\frac{dz}{\rho^2+z^2} \right) \Big|_{\rho^2=R_{shell}^2-z^2}^{\rho=+\infty} = \int_{z=-R_{shell}}^{z=R_{shell}} \frac{q^2}{32\pi\epsilon_0\epsilon_2} \left(\frac{dz}{R_{shell}^2} \right) = \frac{q^2}{32\pi\epsilon_0\epsilon_2} \frac{2}{R_{shell}} \quad (13)$$

Third term of the relation (11) is

$$\int_{z=R_{shell}}^{z=+\infty} \frac{q^2}{32\pi\epsilon_0\epsilon_2} \left(-\frac{dz}{\rho^2+z^2} \right) \Big|_{\rho=0}^{\rho=+\infty} = \int_{z=R_{shell}}^{z=+\infty} \frac{q^2}{32\pi\epsilon_0\epsilon_2} \left(\frac{dz}{z^2} \right) = \frac{q^2}{32\pi\epsilon_0\epsilon_2} \frac{1}{R_{shell}} \quad (14)$$

Combining all terms we obtain

$$G(solution) = \frac{q^2}{32\pi\epsilon_0 R_{shell}} \left(\frac{1}{\epsilon_1} + \frac{2}{\epsilon_2} + \frac{1}{\epsilon_2} \right) = \frac{q^2}{8\pi\epsilon_0 R_{shell}} \left(\frac{1}{4\epsilon_1} + \frac{3}{4\epsilon_2} \right) \quad (15)$$

This leads to the effective value of the average dielectric permittivity

$$\frac{1}{\epsilon} = \frac{1}{4\epsilon_1} + \frac{3}{4\epsilon_2} \quad (16)$$

This confirms that electrode surface and SEI may be considered as 1/4 of the solvated ion surrounding.

Notes and references

- [1] P. Jankowski, J. M. G. Lastra and T. Vegge, *Batteries and Supercaps*, 2020, **3**, 1350–1359.
- [2] J. Kerr, *Philosophical magazine and Journal of science*, 1875, **50**, 337.
- [3] M. J. Aroney, M. R. Battaglia, R. Ferfaglia, D. Millar and R. K. Pierens, *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics*, 1976, **72**, 724–726.