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Electrochemical Isotope Effect and Lithium Isotope Separation

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The electrochemical separation of lithium isotopes is of growing interest due to the need for pure ^{6}Li and ^{7}Li isotopes in the nuclear industry.[1] Here we present results showing a large lithium isotope separation due to electrodeposition. The fractionation is tunable as a function of the overpotential (η) used to plate the metal and can be explained by an electrochemical isotope effect[2,3] that combines Marcus charge-transfer theory[4] with stable isotope theory.[5,6]

Samples of metallic lithium were plated from solutions of 1 M $LiClO_4$ in propylene carbonate (PC) on planar nickel electrodes (~60 mm^2 surface area). All solutions were stirred at a uniform rate with a magnetic stir bar. Table 1 summarizes the electrochemical conditions used to control the reaction:

$$LiClO_{4(PC)} + e^- = Li_{(s)} \qquad E^\circ = -2.98 \text{ V vs NHE}$$

Efficient deposition (31−46%) of lithium was observed and used to adjust the currents plotted in Figure 1. An exchange current (i_0)[7] of ~ −0.34 mA can be extrapolated from the intercept of the fit (dash line, Figure 1) at $\eta = 0$ V, and the slope of the fit yields a transfer coefficient[7] of ~0.175.

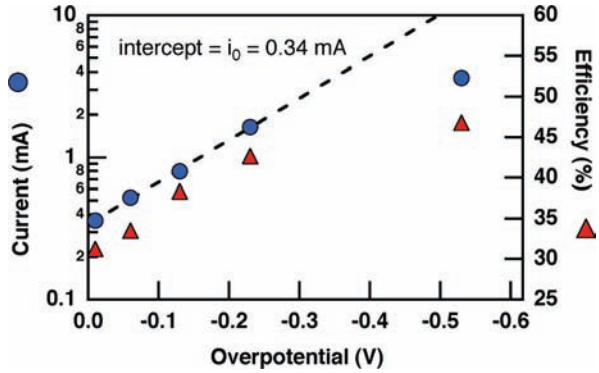

Figure 1. Current and deposition efficiency as a function of applied overpotential. The exchange current, i_0, is extrapolated from a linear fit (dashed line) through the intercept of ln(i) at 0 V.

Samples of electroplated $Li_{(s)}$ and $LiClO_4$ used for preparing stock solutions were dissolved in acid and purified on cation exchange columns. Ratios of ^{7}Li/^{6}Li were then measured on a Nu-Plasma MC-ICP-MS (see Supporting Information). The isotopic compositions of the samples, in reference to the composition of the $LiClO_4$ stock solution (Δ^7Li), are reported in Table 1. The light lithium isotope (^{6}Li) is preferentially partitioned into the metal in all samples with a measured fractionation ranging from $\Delta^7\text{Li} = -21.6$ to −30.5‰. Other experimental investigations[8] of the lithium isotope exchange reaction determined a fractionation factor of 1000 ln $\alpha_{\text{solid–solution}} = -29.6$‰ for the system under study here, an identical result to the fractionation measured here closest to equilibrium ($\eta = -0.01$ V, $\Delta^7\text{Li} = -29.6$‰). Figure 2 shows that the observed fractionation systematically decreases as the applied overpotential increases from $\eta = -0.01$ to −0.53 V.

In a series of papers Kavner et al. (2005, 2008)[2,3] derive an equation predicting isotopic fractionation due to an electrochemical isotope effect (α_{EIE}), defined by the ratio of electron transfer rates (k'/k) for isotopically substituted species (prime for heavy isotopologues):

$$\ln \alpha_{EIE} = \ln\left(\frac{k'}{k}\right) = \ln\left(\frac{\nu'}{\nu}\right) + \left(\frac{\Delta G^* - \Delta G^{*\prime}}{k_B T}\right)$$
$$= \frac{1}{2}\ln\left(\frac{m}{m'}\right) + \left(\frac{\ln \alpha_{eq}}{2} - \frac{k_B T(\ln \alpha_{eq})^2 + 2k_B T \ln(Q_P/Q_R) \ln \alpha_{eq} + 2\eta z e \ln \alpha_{eq}}{4\lambda}\right) \quad (1)$$

where ν, ΔG, k_B, T, m, α_{eq}, Q_P/Q_R, z, e, and λ denote collision frequency, activation free energy, Boltzmann's constant, temperature, mass in motion, equilibrium fractionation factor, partition function ratio of abundant isotopologues of product (P) and reactant (R), number of electrons, charge of electron, and Marcus reorganization energy, respectively.

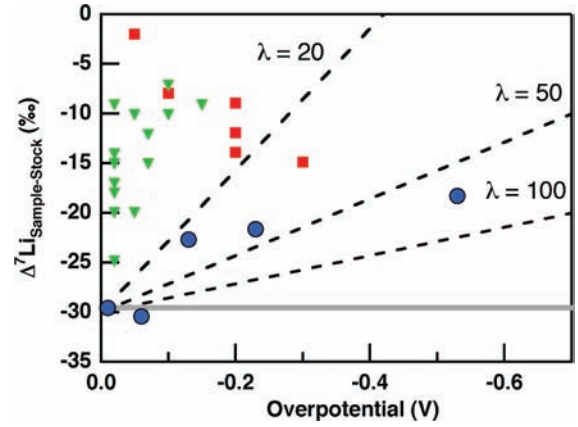

Figure 2. Lithium isotope fractionation vs overpotential. This study (blue circles); intercalated Li in tin[9] (red squares), graphite[10] (green triangles); measured equilibrium fractionation (gray solid line[8]); and calculated electrochemical isotope effect (dashed lines[2,3]) as a function of Marcus reorganization energy (labeled λ in kJ mol^{-1}).

Equation 1 predicts that the magnitude of isotopic fractionation is a linear function of the applied overpotential and that its slope is proportional to the equilibrium fractionation factor between product and reactant divided by the Marcus reorganization energy. Large

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Table 1. Summary of Electrochemical Parameters and Isotopic Fractionation

sample	overpotential, η (V)	charge delivered (C)	time taken (s)	average current (mA)	mass plated[a] (μg)	deposition rate (mol/m^2 s)	deposition efficiency[a] (%)	Cottrell current[b] (mA)	isotopic fractionation[c] Δ^7Li $\pm$ 2σ (‰)
Li_01	−0.01	−0.1	85.6	−1.17	2.2	5.8×10^{-5}	31	−4.19	−29.6 ± 0.5
Li_02	−0.06	−0.1	63.2	−1.58	2.4	7.9×10^{-5}	33	−5.16	−30.4 ± 0.5
Li_03	−0.13	−0.1	47.6	−2.10	2.7	12.0×10^{-5}	38	−5.96	−22.7 ± 0.5
Li_04	−0.23	−0.1	25.8	−3.88	3.0	25.1×10^{-5}	42	−7.96	−21.6 ± 0.5
Li_05	−0.53	−0.1	12.8	−7.81	3.3	55.5×10^{-5}	46	−11.30	−18.3 ± 0.5

[a] The mass of lithium deposited was estimated from the dilution factors and concentrations of Li measured on the MC-ICP-MS; this was used to determine the overall deposition efficiency. [b] Cottrell currents[7] are calculated using a diffusion coefficient reported in the literature[11] of 1.2×10^{-10} m^2 s^{-1}. [c] $\Delta^7\text{Li} = [(^7\text{Li}/^6\text{Li})_{\text{Sample}}/(^7\text{Li}/^6\text{Li})_{\text{Stock}}]*1000$ in per mil.

electrochemical isotope fractionations have been observed in the transition metals Fe(II)[2] and Zn(II).[3] The light metal Li(I) is expected to produce a stronger electrochemical effect, allowing a more sensitive test of the parameters in eq 1.

Using the reported $1000 \ln \alpha_{eq} = -29.6‰$,[8] and assuming an $\ln(Q_P/Q_R) = 1$ (a small contribution regardless) and an estimate for (m/m') that normalizes the value of $\Delta^7\text{Li} = 1000 \ln \alpha_{eq}$ at $\eta = 0$ V, the variation of Δ^7Li with η has been calculated at 25 °C for various reorganization energies. Figure 2 shows that the range $\lambda = 20$ to 100 kJ/mol encompasses the trends seen in the experimental data.

The equilibrium isotopic fractionation between Li^+ in solution and metallic Li can be predicted using *ab initio* molecular modeling techniques for calculating the vibrational energy difference between isotopologue species.[5,6] Lithium forms a tetrahedral complex bound to four propylene carbonate (PC) molecules via oxygens in the 1 M $LiClO_4$ stock solutions.[12] Calculation of the reduced partition function ratio (for ^{7}Li/^{6}Li) of metallic lithium from a vibrational (phonon) density of states[13] and for a tetrahedrally coordinated Li complex from *ab initio* studies[14] yields a fractionation factor of $1000 \ln \alpha_{\text{solid-solution}} = -37.5‰$ (see Supporting Information). This is in reasonable agreement with the previously measured equilibrium fractionation factor,[8] which agrees with our independent result at the overpotential closest to equilibrium ($\eta = -0.01$ V). The predictions of eq 1 suggest that the equilibrium fractionation factor is a strong control over electrochemical isotope fractionation, and therefore, *ab initio* studies may be a useful tool for determining a baseline fractionation for a chemical system.

Higher overpotentials may also drive the reaction kinetics into a regime where the supply of Li^+ to the electrode surface may become diffusion limited. A qualitative description of the mass-transport regime can be calculated by taking the ratio of observed current to the calculated rate-limiting Cottrell current[7,15] (reported in Table 1). Figure 3 plots lithium isotope fractionation as a function of this current ratio and the deposition rate of lithium (built into this ratio) with results similar to those seen in previous studies of iron and zinc[15] where fractionation decreases as the fraction of measured current to Cottrell diffusion-limiting current increases. This trend is consistent with a measurement of diffusive fractionation of lithium ions in aqueous

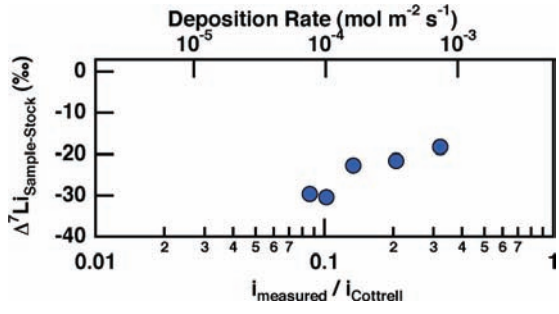

Figure 3. Li isotope fractionation as a function of deposition rate and the measured current to Cottrell diffusion-limiting current ratio.

systems, with a reported ratio $D_{7\text{Li}}/D_{6\text{Li}} = 0.99772$,[16] yielding $\Delta^7\text{Li}_{\text{diffusion}} \approx -1.14‰$ at the electrode.[15] All samples lie well below a current ratio of 1 ($i_{\text{measured}}/i_{\text{Cottrell}} = 0.09$ to 0.32) indicating that conditions are not mass-transport limited. To distinguish between mass transport and electrochemical explanations for the observed voltage dependent effect, further studies are needed to investigate the trends in Li isotopic fractionation close to equilibrium.

Both isotopes of Li have important applications in the nuclear industry. Previous studies have focused on the electrochemical intercalation of lithium into various electrode materials (e.g., Hg,[17] graphite,[10] Ga,[1] Sn,[9] and Zn[18]) producing fractionations on the order of −2 to −60‰. The largest fractionations are seen in Li(Hg) amalgams plated at overpotentials of up to −7.2 V.[17] This study demonstrates a new and simple method to achieve large Li isotope separations without the environmentally disruptive Hg amalgamation.

This work together with earlier studies on isotope fractionation during plating of Fe[2] and Zn[3] demonstrate large isotope fractionations due to electroplating. These results are consistent with the hypothesis of eq 1 predicting isotope fractionations resulting from electrochemical reactions.

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Supporting Information Available: Materials and Methods; Table S1; Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Zenzai, K.; Yanase, S.; Zhang, Y.-H.; Oi, T. *Prog. Nucl. Energy* **2008**, *50*, 494–498.
(2) Kavner, A.; Bonet, F.; Shahar, A.; Simon, J.; Young, E. *Geochim. Cosmochim. Acta* **2005**, *69*, 2971–2979.
(3) Kavner, A.; John, S. G.; Sass, S.; Boyle, E. A. *Geochim. Cosmochim. Acta* **2008**, *72*, 1731–1741.
(4) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679–701.
(5) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261–7.
(6) Urey, H. C. *J. Chem. Soc.* **1947**, 562–81.
(7) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons, Inc.: New York, 2001.
(8) Singh, G.; Hall, J. C.; Rock, P. A. *J. Chem. Phys.* **1972**, *56*, 1855–62.
(9) Yanase, S.; Oi, T.; Hashikawa, S. *J. Nucl. Sci. Technol.* **2000**, *37*, 919–23.
(10) Yanase, S.; Hayama, W.; Oi, T. *Z. Naturforsch.* **2003**, *58a*, 306–312.
(11) Nishikawa, K.; Fukunaka, Y.; Sakka, T.; Ogata, Y. H.; Selman, J. R. *J. Electrochem. Soc.* **2006**, *153*, A830-A834.
(12) Li, T.; Balbuena, P. B. *J. Electrochem. Soc.* **1999**, *146*, 3613–3622.
(13) Staikov, P.; Kara, A.; Rahman, T. S. *J. Phys.: Condens. Matter* **1997**, *9*, 2135–2148.
(14) Yamaji, K.; Makita, Y.; Watanabe, H.; Sonoda, A.; Kanoh, H.; Hirotsu, T.; Ooi, K. *J. Phys. Chem.* **2001**, *105*, 602–613.
(15) Kavner, A.; Shahar, A.; Black, J. R.; Young, E. *Chem. Geol.* **2009** (in press), doi:10.1016/j.chemgeo.2009.04.018.
(16) Richter, F. M.; Mendybaev, R. A.; Christensen, J. N.; Hutcheon, I. D.; Williams, R. W.; Sturchio, N. C.; Beloso, A. D. J. *Geochim. Cosmochim. Acta* **2006**, *70*, 277–289.
(17) Fujie, M.; Fujii, Y.; Nomura, M.; Okamoto, M. *J. Nucl. Sci. Technol.* **1986**, *23*, 330–7.
(18) Mouri, M.; Yanase, S.; Oi, T. *J. Nucl. Sci. Technol.* **2008**, *45*, 384–389.

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