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Electrochemical Lithium Deposition

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Microcalorimetric Measurements of the Solvent Contribution to the Entropy Changes upon Electrochemical Lithium Bulk Deposition**

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Research on the deposition of lithium from organic electrolytes has been pursued very thoroughly since the development of the lithium-ion battery.[1] Although graphite has replaced lithium metal as anode material owing to safety and performance issues, the deposition of lithium is still a major concern. During the charging of the battery, lithium ions are intercalated into the graphite lattice. There are however various factors that may lead to the deposition of lithium on the electrode instead of intercalation. Low temperature and high current density are among the main reasons for lithium plating.[2] Dendritic growth of lithium in turn can lead to a short-circuit fault of the cell and a thermal runaway of the battery.

Electrochemical microcalorimetry can help to shed some light on the thermodynamic aspects of lithium deposition. Because electrical work is performed during this reaction, the exchanged heat is not linked to the enthalpy of the reaction but to the entropy, as stated already by Onsager and discussed in detail, for example, by Agar.[3] We measured the temperature change on the back side of a thin electrode during short periods of bulk deposition of lithium. This allows us to quantitatively determine the reversible heat change accompanying the reaction. The heat, usually referred to as Peltier heat, corresponds to the entropy of reaction, which includes contributions from all species involved in the half-cell reaction. We studied the lithium bulk deposition in a typical battery electrolyte, $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC). In this electrolyte the entropy of Li bulk deposition is dominated by entropy changes from solvation of Li^+. Within a simple model we derived the coordination number of Li^+ in the EC/DMC mixture.

First quantitative measurements of the Peltier heat of single electrode reactions date back to the beginning of the 20th century (see for example Ref. [4] for a compilation of early data). Most of those studies concentrated on bulk metal deposition, for example, of Ag, Cu, Cd, and Zn from aqueous solutions. With experimental improvements, reliable data also became available for electron-transfer reactions, for example, for $[Fe(CN)_6]^{4-/3-}$.[5] Also the influence of cations and anions and their transport processes on the heat changes was studied in detail (see for example Refs. [5a,6]). Battery-related systems came into focus with the work of Conway and coworkers,[7] who calorimetrically studied Zn and bromine electrodes to gain understanding of the thermal behavior of battery charge and discharge processes. Most research on reversible heat changes of battery related single electrode reactions concentrated on the hydrogen evolution reaction (see for example Ref. [8] and references therein). Very little work has been performed on Li-ion batteries, mostly considering complete cells.[9] Maeda studied the heat change of a single graphite electrode upon intercalation of ClO_4^-, BF_4^-, K^+, and Li^+.[10] Unfortunately the sensitivity of the calorimetric setup was insufficient to quantitatively measure the Peltier heat of the Li intercalation process. It should be noted that all of the above cited studies required rather high electrochemical conversions of the order of several 10 to 10000 monolayers, referenced to the electrode surface, to obtain reliable heat measurements. Only recently reactions with submonolayer conversions, such as oxide formation on a Au surface,[11] hydrogen adsorption on a platinized Pt foil,[12] or Cu underpotential deposition on a Au surface,[13] became accessible. Herein we apply our microcalorimetric approach[14] to the study of Li deposition. As heat changes upon deposition or dissolution down to a few percent of a monolayer of Li can be reliably determined with this method, we were able to directly measure the reversible entropy change of the Li electrode.

Prior to the calorimetric experiments, we deposited a thick Li layer (ca. 1800 monolayers) on a Ni working electrode. Subsequently, pulsed Li deposition and dissolution was conducted on that surface. Figure 1 shows the potential, current, and temperature transients during a typical experiment. At 10 ms, a potential pulse with amplitude -50 mV starting at the Li^+/Li equilibrium potential, that is, with -50 mV overpotential, was applied for 10 ms. At the end of the pulse, at $t=20$ ms, the external cell current was interrupted by an electronically operated switch. The potential then relaxed towards the Li^+/Li equilibrium potential. During the negative potential pulse we measured a negative current, which corresponds to the deposition of lithium. The corresponding charge can be retrieved by integration of the current transient and amounts to 6.3 μC in the shown experiment. This is 20% of a monolayer of Li assuming a surface density of 10^{15} atoms cm^{-2} for Li. The temperature signal started to drop immediately with the beginning of the pulse, that is, with the beginning of Li deposition. After the end of the pulse the

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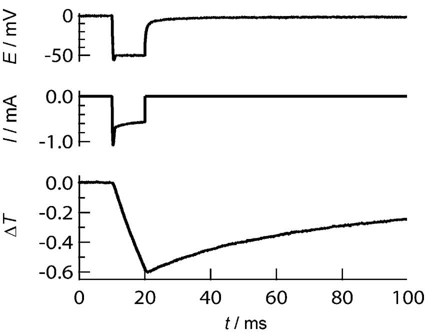

Figure 1. Potential (top), current (middle), and temperature (bottom) transients of a typical pulse experiment. Lithium deposition was conducted on a circa 1800 monolayer-thick Li-film on Ni by a 10 ms -50 mV pulse at $t=10$ ms. This led to cooling of the electrode. At $t=20$ ms the outer circuit was switched off and the temperature equilibrated on a timescale of several 100 ms.

decrease continued for a short time (ca. 2 ms) before the temperature relaxed to its equilibrium value. The temperature change during the Li deposition pulse directly reflects the exchanged heat during the process. From this temperature change we quantitatively determined this heat change by calibration of the calorimeter with the $[Fe(CN)_6]^{4-/3-}$ reaction (for details, see Ref. [14]).

The experiment was repeated with different pulse amplitudes, that is, overpotentials, for the Li deposition and dissolution. The measured heat changes, normalized by the charge of the Faradaic process, that is, the conversion of Li for the respective pulse experiment, are depicted in Figure 2.

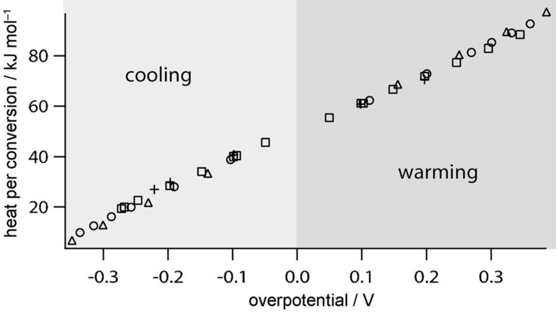

Figure 2. Plot of the normalized heat, that is, heat per conversion, versus overpotential of the reaction. The calculated heat is normalized by the conversion, with positive conversion corresponding to positive cell current. Data of four series of pulses recorded consecutively. To separate the reversible heat effect from irreversible effects that are due to overpotential, we extrapolated to zero overpotential.

Note our sign convention, which is negative charge and hence negative conversion for Li deposition at negative overpotential and, vice versa, positive charge and hence positive conversion for Li dissolution at positive overpotential. The heat change is counted negatively when the electrode temperature decreases. Upon Li deposition (negative overpotential), a positive heat per conversion corresponds hence to a decrease of the electrode temperature.

For positive potential pulses we detected warming, whereas for negative potential pulses we detected cooling of the electrode (Figure 2), reflecting the reversibility of the process. With increasing absolute value of the overpotential, that is, stronger deviation from equilibrium, the system becomes less cold for deposition, or warmer for the dissolution process, respectively.

To discuss these results, the contributions to the heat effects upon electrochemical reactions have to be considered in more detail. The heat effects are due to two major contributions: 1) Reversible heat from the electrochemical reaction, that is, Peltier heat; and 2) irreversible heat while driving the reaction.[3,6a] In our case irreversible heat effects mostly stem from deviation from thermal equilibrium upon driving the electrochemical reaction with the overpotential η.[15] Joule heat, caused by the current flow through the electrolyte, is not measured in our experiment owing to the short pulses and low heat conductivity of the electrolyte.[14] The reversible heat effects reflect the molar entropy change ΔS upon the electrochemical reaction, which includes the molar entropy of the electrochemical reaction itself as well as of possible side reactions and changes in entropy due to transport of ions and electrons upon current flow.[3] Thus the change of heat δq can be written as:

$$\delta q = T\Delta S\,\mathrm{d}\xi - |\eta|\, n_e F\,\mathrm{d}\xi$$

with the temperature T, reaction variable ξ of the reduction reaction, Faraday constant F, overpotential η, and stoichiometric number of electrons involved in the reaction n_e. δq becomes negative when heat is transferred from the system to the surrounding. The reversible contribution to the heat, that is, the heat change in the limit of vanishing overpotential, is called Peltier heat, in analogy to the heat effects at isothermal junctions of two different electronic conductors upon current flow. The corresponding molar heat $T\Delta S$ is named Peltier coefficient Π. Extrapolation of the data shown in Figure 2 to zero overpotential gives a reversible heat change of $50\,\mathrm{kJ\,mol^{-1}}$. The average value from altogether 23 pulse series is $\Pi = 48 \pm 2\,\mathrm{kJ\,mol^{-1}}$. We expect an additional error of the order of $5\,\mathrm{kJ\,mol^{-1}}$ originating from the calibration.

Contributions due to the transport of ions and electrons upon current flow, that is, corrections for the Eastman heat of transport, can be neglected in the present case (see the Supporting Information). The determined Peltier heat directly reflects the reaction entropy of the Li deposition process, which amounts to $\Delta_R S \approx \Pi/T \approx 165\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Compton and co-workers derived entropies for the deposition of Li from tetrahydrofuran by temperature dependent measurements of the half-cell potential versus a ferrocene reference electrode. A value of $-89 \pm 5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is given. However, as this value includes the entropy change of the complete cell reaction and was not corrected for the temperature dependence of the reference electrode, it cannot be directly compared with our measurement.[16]

Positive entropy of reaction for the deposition of lithium, as found in our study, is counterintuitive at first sight, because dissolved mobile Li^+ ions are expected to have higher entropy than atoms in the solid phase. The entropy change upon immobilization of Li^+ ions, ΔS_{Li}, is therefore expected to be negative. This description however fails to consider the solvation shell of the ion. Strong solvation decreases the degrees of freedom of solvate molecules and thus implies an entropy decrease upon solvation of Li^+. In fact immobilization of solvent molecules in the solvation shell is usually the dominating contribution to the entropy of solvation. This concept was first proposed by Ulich about 80 years ago to calculate the solvation number of ions in water.[17] He essentially assumed that the water in the first solvation shell of the ion is immobilized similarly to water in an ice crystal. Later Marcus adopted this approach for the determination of solvation numbers in non-aqueous solvents.[18] He split the solvation entropy, that is, the entropy change upon transferring an ion from an ideal gaseous state into a solvent, into three parts. First, the contribution from transfer of the ion from its gaseous state into the liquid state, with all interactions switched off. This corresponds to the change of the volume at the disposal of the ion in an ideal gas. The corresponding entropy change can be readily calculated. The second contribution is the entropy change by immobilization of solvent ions in the first solvation shell, ΔS_{immob}. The third part corresponds to the entropy change from effecting solvent molecules beyond the first solvation shell. Marcus estimated the latter contribution, ΔS_{Born}, by the Born equation, regarding the electrostatic interaction of the ion with a structureless solvent characterized by its dielectric constant. Thus ΔS_{immob} could be readily calculated from the values of the solvation entropy. As it is assumed that the solvent molecules in the first solvation shell are immobilized similar to molecules in the frozen state, the coordination number can be calculated by dividing ΔS_{immob} by the entropy of freezing of the solvent, extrapolated to the respective temperature.

In our experiment, we directly measure the reaction entropy for bulk Li deposition, which is made up of the entropy change upon immobilization of a Li^+ ion, ΔS_{Li}, disregarding the interactions with the solvent, and the entropy change from solvation. Adopting Marcus' notation and considering that ΔS_{immob} and ΔS_{Born} are liberated upon Li deposition, the reaction entropy can be written according to Equation (1):

$$\Delta_R S = \Delta S_{\text{Li}} - \Delta S_{\text{immob}} - \Delta S_{\text{Born}} \tag{1}$$

It should be noted that we disregarded the entropy of the electrons in the electrode, which, however, is usually small compared to the ionic entropy.[3] ΔS_{Born} can be estimated from the radius of the ion including the first solvation shell, the relative permittivity of the solvent and its temperature dependence. With the data of Ref. [19], we calculated $\Delta S_{\text{Born}} = -3.1\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ for 1 M Li^+ in ethylene carbonate. For a 1:1 mixture of EC and DMC $\Delta S_{\text{Born}} = -16\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, which is slightly larger, owing to the lower relative permittivity of the mixture. For this calculation we assumed that the temperature dependence of the permittivity of the mixture is the same as for pure EC. The permittivity of 1:1 EC/DMC is about half of that of pure EC, as we determined by capacitance measurements between two Pt electrodes immersed into the dielectric at frequencies between 10 kHz and 1 MHz. The measurement was calibrated by determining the capacitance of water in the same cell.

The entropy loss due to Li immobilization, ΔS_{Li}, can be estimated similarly to the immobilization entropy of the solvent from the melting entropy of Li. At its melting point of 453.69 K, the molar entropy of melting of Li amounts to $10.2\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$.[20] This value was extrapolated to room temperature, assuming an average difference between the heat capacities of solid and liquid Li of $7.1\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$,[20,21] and corrected for the change in volume at the disposal of the ion from liquid Li to 1 M solution.[19,20] This results in a contribution to the reaction entropy from immobilization of Li^+ ions of $\Delta S_{\text{Li}} \approx -42\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. It should be noted that in this calculation a reduction of the entropy of Li in its melt by local structuring is disregarded. This would, however, lower the entropy loss upon immobilization of Li^+. Considering $\Delta S_{\text{Born}} \approx -16\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, as calculated above, our measurements result in an entropy change, which is due to the immobilization of solvent molecules in the inner solvation shell of the Li^+ ion in LP30 of $\Delta S_{\text{immob}} \approx -192\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. From this value we can derive the coordination number in the inner solvation shell following the procedure of Ulich and Marcus. The freezing entropy of DMC is $-41.6\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$, that of EC is $-41.8\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$.[22] Assuming a similar value for the 1:1 mixture of EC and DMC as used in our experiments we calculate a coordination number of Li^+ of $n \approx 4.6$ in the inner solvation shell.

The coordination number of lithium in EC/DMC mixtures has been determined by several methods. Raman spectroscopy has been used to study the dependency of the intensity of the ring breathing mode on lithium concentration.[23] The temperature dependency of the impedance resistance corresponding to desolvation has been studied with electrochemical impedance spectroscopy in solvents with different EC:DMC ratios.[24] Electrospray ionization-mass spectroscopy was used to determine the coordination number in several organic solvents.[25] Theoretical studies, including DFT and Hartree–Fock methods, calculated the energy of solvation.[23b,26] Those studies reported coordination numbers of Li^+ between 3 and 5 in carbonate solvents such as EC and DMC. Thus the coordination number of 4.6 extracted from our calorimetric experiment is in good agreement with that obtained by the other methods. It should be noted that our number includes only molecules in the inner solvation shell. However, also the cited Raman measurements and the calculations disregard higher-order solvation shells.

In conclusion, the entropy change upon electrochemical deposition of Li from EC/DMC mixtures was directly determined by electrochemical microcalorimetry. The reaction entropy of the deposition reaction is strongly positive and it is dominated by the release of solvent molecules from the solvation shell of the Li^+ ion, which leads to considerable cooling of the electrode in our adiabatic calorimeter. A coordination number of 4.6 was derived from our measurements, which is in accordance with calculations and experiments. It should be emphasized that the entropic contribution to the Gibbs Free energy of the half-cell reaction amounts to about $48\,\text{kJ}\,\text{mol}^{-1}$, which corresponds to about 0.5 V of the half-cell potential.

Finally, we wish to make a comment on an important practical aspect of our result. Decreasing temperature enhances the risk of lithium plating on negative carbon electrodes in lithium-ion batteries. A possible consequence of the cooling effect detected here is that, on spots where lithium plating occurs, the local temperature would further decrease, accelerating thus the detrimental lithium plating and threatening thus the safety of the entire battery.

Experimental Section

An electrochemical microcalorimeter in an argon-filled glove box was used for the experiments (for details, see Refs. [14,27]). The calorimeter consisted of a 50 μm-thick Ni sheet in close thermal contact with a gold-coated pyroelectric polyvinylidene fluoride (PVDF) foil as a temperature sensor. Temperature changes of the Ni electrode could be measured at the back side of the electrode with a delay of only a few 100 μs (this concept was introduced for the measurement of the heat of adsorption at the back side of a thin sample in UHV studies;[28] PVDF foil has also been used as a pyroelectric temperature sensor).[29] To obtain optimal contact of the Ni sheet and the PVDF foil, the air between them was removed and the electrode assembly was pressed together by ambient pressure. The electrochemical cell was mounted on top of the Ni sheet and sealed with an O-ring. The active electrode area of the Ni sheet, which served as working electrode, was about $0.2\ \mathrm{cm}^2$. Platinum wire was used as counter and quasi-reference electrode. To prevent heat loss into the cell assembly and electrolyte we applied only short pulses of 10 ms duration to drive the electrochemical reaction. On this timescale, the heat loss into the electrolyte and the set-up is very low while the electrode–sensor assembly is already close to thermal equilibrium. The temperature change of the electrode during the pulse is therefore proportional to the heat generated by the electrochemical reaction. The data were calibrated by the heat generation of the well-studied one-electron transfer reaction of a 0.1 M $[Fe(CN)_6]^{4-}$/0.1 M $[Fe(CN)_6]^{3-}$ aqueous solution, for which the Peltier heat is available.[5a]

The electrolyte for all experiments was 1 M $LiPF_6$ in a 1:1 mixture of EC and DMC (LP30, battery grade, Merck). For the calibration, analytical grade $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ (Merck) and ultrapure water (Arium, Sartorius) were used. The electrode was cut from 50 μm Ni foil, polished with diamond paste (dia-plus, Walter Messner GmbH), and cleaned with ultrapure water and acetone (Merck, p.a.). We used a nickel electrode for the Li bulk deposition experiments because Ni is one of the few metals that do not form an alloy with lithium.[30] Prior to the calorimetric experiment, ca. 1800 monolayers (ML) of Li were electrochemically deposited in situ on the Ni sheet. This changed the Li concentration of the cell electrolyte by about 0.2 %, which was negligible for the present study. To minimize the influence of the ohmic potential drop on the reference potential, the shaft of the platinum quasi-reference electrode was coated with a Teflon tube and the reference electrode was mounted in close proximity to the working electrode. All of the given potentials are referenced to the Li^+/Li equilibrium potential in the CV. Experiments generally started with the calibration of the setup. Afterwards the cell was thoroughly rinsed with ultrapure water and analytical-grade acetone. The setup was subsequently flange-mounted to the glove box and dried by evacuation with a turbomolecular pump to $p \approx 10^{-5}$ mbar before the calorimetric measurements involving the $LiPF_6$ electrolyte were carried out. Cyclic voltammetry measurements were used to inspect the electrochemical properties of the cell and to rule out contamination by traces of water and oxygen (see the Supporting Information).

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