
GALVANOSTATIC STUDY OF THE KINETICS OF LITHIUM DEPOSITION ON PLATINUM ELECTRODE IN DIMETHYLFORMAMIDE

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

The deposition of lithium in dimethylformamide (DMF) has been studied by means of galvanostatic measurements. The overpotential was recorded during constant current pulses of so short a duration that only a few monolayers per pulse were deposited. The experiments were carried out under conditions of minimum contamination of the metal surface. The deposition process of Li in DMF is irreversible, the electron transfer being the rate-determining step. A mechanism of Li electrodeposition in DMF was proposed.

Most information about electrodeposition of lithium in nonaqueous electrolytes refer to the mercury electrode¹⁻³; the scarcity of data referring to solid electrodes is due to the difficulty in controlling the quality of the electrode surface during the experiments. This difficulty was overcome by using the galvanostatic method with d.c. transients. The solvent chosen in the present work was dimethylformamide because of its wide electroinactivity range⁴ and because the solubility of many salts in it is higher than in other solvents. The deposition kinetics was studied on Pt electrodes by the galvanostatic method.

EXPERIMENTAL

The apparatus comprised a PARC model 273 potentiostat, an APPLE II microcomputer, and an FX-100 printer. The pulse generator was provided with a switch giving a rise time of the polarizing current of less than 4 μ s. A series of overpotential-time curves at various current densities was recorded; each η - t curve was obtained with a single pulse of the polarizing current. The η - t data were transferred to an APPLE II microcomputer and could be printed with the FX-100 printer.

The cell resembled that described earlier⁵. The working electrode was prepared from a Pt rod of 99.99% purity with a diameter of 0.4 cm. The electrode was carefully sealed with Teflon

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leaving only the working surface exposed to the solution. The electrode was mechanically abraded before the measurements with successively finer grades of emery paper (first 600 and finally 1 200) to a mirror finish and then washed in acetone and in the working solution. The same electrode was used in every experiment after polishing and washing as indicated. The counter electrode was a Pt black electrode and the reference, against which the potentials reported here are referred, was Ag/AgCl electrode connected with a salt bridge.

The method of Brummer⁶ was adopted for the purification of DMF. The concentration of water in the purified solvent, as determined by gas chromatography, was less than 10 ppm (v/v).

LiClO₄ of analytical reagent grade was dried in vacuum before use. The electrolyte was 0.2M LiClO₄ in DMF. The solutions were deaerated by bubbling helium taken from a normal tank supply and purified from traces of CO, CO₂, O₂, and H₂O. The purification train also contained three liquid-nitrogen traps with active carbon mainly for the removal of traces of organic impurities in the gas. To prevent water vapour from entering the system, a special dry box was used⁵. All experiments were done at ambient temperature, i.e. 290 ± 2 K.

RESULTS AND DISCUSSION

Relation Between Overpotential and Time

A typical η - t curve is shown in Fig. 1. The cathodic transients did not show a clear steady-state value, suggesting that the deposition of lithium on Pt electrode in DMF is irreversible⁷. In another experiment, a rapid sweep was used to determine the slope of the η - t curve (Fig. 2); the double layer capacitance, C , was calculated as

$$C = |i(dt/d\eta)_{t \rightarrow 0}|. \quad (1)$$

The value for platinum electrode was 26.8 $\mu\text{F}/\text{cm}^2$, whereas typical values for Hg electrode in aqueous electrolytes in the negative potential region are 16–18 $\mu\text{F}/\text{cm}^2$.

Relation between Overpotential and Current Density

The relation between the activation overpotential, η , and current density, i , is given by

$$i = i_0 [\exp(-\alpha_c \eta_c F/RT) - \exp(\alpha_a \eta_a F/RT)], \quad (2)$$

where i_0 is the exchange current density, α_c the cathodic transfer coefficient, α_a the anodic transfer coefficient, and other symbols are as usual. For monovalent ions and $\eta_c > 40$ mV, we obtain the Tafel equation

$$\eta_c = -2.303 (RT/\alpha F) \log i_0 + 2.303 (RT/\alpha F) \log i. \quad (3)$$

A plot of the experimental activation overpotential against $\log i$ (i in mA per cm^2) gives a straight line, whose extrapolation to $\eta_c = 0$ gives $i_0 = 8.8 \cdot 10^{-4}$ mA cm^{-2} . The transfer coefficient α_c was calculated from Eq. (3) as 0.13. The value of i_0 shows that the electrodeposition of lithium in DMF is irreversible.

A simple discussion is possible if the Pt surface is not highly covered with adions. If we assume that



then

$$v_1 = k_1 c(M^{z+}) \exp(-\beta z \Delta\Phi F/RT), \quad (5)$$

$$v_{-1} = k_{-1} c(M_{ad}) \exp[(1 - \beta) z \Delta\Phi F/RT], \quad (6)$$

where v_1 and v_{-1} are the rates of the forward and backward reactions, $\Delta\Phi$ is the Galvani potential difference between the metal and the solution, β is the symmetry factor, c is concentration and k_1 , k_{-1} are rate constants.

The electron transfer is succeeded by a rate-determining step. Hence, $v_1 = v_{-1}$ and

$$c(M_{ad}) = (k_1/k_{-1}) c(M^{z+}) \exp(-z \Delta\Phi F/RT). \quad (7)$$

Let us assume that more than one (consecutive) step takes place after the electron transfer. Before the rate-determining step (9), each process is in equilibrium:



Here, P is adion and R is final product. Then

$$c_p = K_2 c^m(M_{ad}), \quad (10)$$

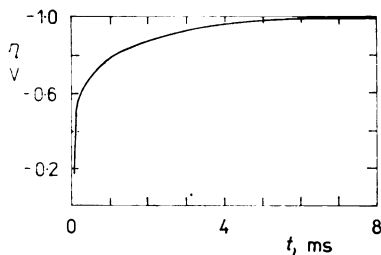


FIG. 1

η - t Curve for electrodeposition of Li on a Pt electrode ($i = 2 \cdot 10^{-4}$ A) in 0.2M LiClO₄

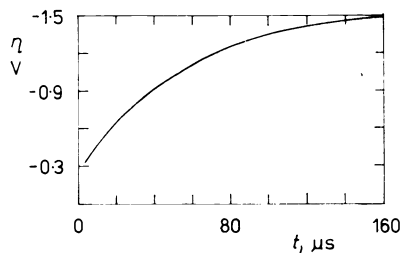


FIG. 2

η - t Curve for electrodeposition of Li on a Pt electrode in 0.2M LiClO₄; $i = 2 \cdot 10^{-4}$ A

where K_2 is a potential-independent constant and $m \geq 1$. Further

$$v_{\text{depn}} = k_3 c_p^p, \quad (11)$$

where $p \geq 1$. Hence, with Eqs (7), (10) and (11), the deposition rate will be given as

$$i_{\text{depn}} = \lambda F k_3 K_2^p (k_1/k_{-1})^{mp} c^{mp} (M^{z+}) \exp(-z \Delta\Phi F m p / RT), \quad (12)$$

where λ is the number of elementary charges lost by the metal in the rate-determining step. From Eq. (12) we obtain

$$\partial\Delta\Phi/\partial \ln i_{\text{depn}} = -RT/z m p F. \quad (13)$$

Hence (for $m p > 1$), for the rate-determining chemical step

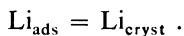
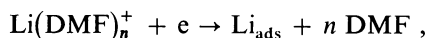
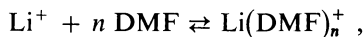
$$\partial\Delta\Phi/\partial \log i_{\text{depn}} \leq 2.303 RT/z F. \quad (14)$$

It may be concluded that if the Tafel slope observed for the deposition of a monovalent cation is less than or equal to 0.06 V at 290 K, the rate-determining step cannot be an electron transfer. The Tafel slope obtained in this work is equal to 0.45, i.e. larger than 0.06.

Comparing the result of this discussion with the experimental η_c - i behaviour, we conclude that the electron transfer is the rate-determining step in the deposition of lithium in DMF.

CONCLUSIONS

The probable mechanism of the deposition of lithium in DMF consists of three reaction steps:



From the η - $\log i$ dependence it follows that $i_0 = 8.8 \cdot 10^{-4} \text{ mA cm}^{-2}$, and the electrodeposition is irreversible, the rate-determining step being the electron transfer.

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