ELECTRODE PROCESSES AT MERCURY IN THE FAR CATHODIC POTENTIAL REGION

II. THE REDUCTION OF Li⁺ AND mM Na⁺ FROM AQUEOUS 1 M LiCI SOLUTION

R. M. REEVES, M. SLUYTERS-REHBACH AND J. H. SLUYTERS Laboratory of Analytical Chemistry, State University, Utrecht (The Netherlands) (Received 21st June 1971)

INTRODUCTION

In a previous paper¹, it was shown that the cathodic electrode process occurring at mercury in 1 M aqueous solutions of Na⁺ and K⁺ is much more complicated than had been thought earlier. It was found that Na⁺ and K⁺ ions are reduced completely reversibly within the limits of both d.c. and a.c. measurements. This reduction process was found to be accompanied by a second, irreversible, reduction process which was interpreted as being due to the chemical reaction of the amalgam, formed by reduction of the alkali metal ion, with water or hydrogen ions.

The cathodic process occurring at mercury in solutions of lithium salts is known to occur at significantly more negative potentials than in solutions of either potassium or sodium salts. It was thought useful to study this process using the same procedures as were employed in the previous paper¹ and to compare the results. As far as we know, the kinetics of the Li⁺ reduction have not been fully investigated previously, except for a study by Imai and Delahay² which, however, was shown to be theoretically in error³.

For reasons discussed in an earlier publication¹, the experiments to be described are carried out in 1 M LiCl solution, in the absence of an indifferent electrolyte. Lithium chloride may, on the other hand, serve as an indifferent electrolyte for a study of the reduction of Na⁺ in mM concentration. Such a study also involves a more negative potential region than that employed when investigating the 1 M sodium system. Using this sytem it is possible to check the generality of the phenomena described above.

EXPERIMENTAL

The experimental methods employed were described fully in the earlier publication¹. They involved d.c. polarography and impedance measurements at a dropping mercury electrode. From the latter measurements, the real and imaginary components of the electrode admittance, Y'_{el} and Y''_{el} were calculated in the usual way. The shielding effect at the dropping electrode was corrected by using the measured value of the solution resistance at each frequency. The analysis of the admittance has been described in detail¹. The relevant features will be mentioned in the subsequent sections when necessary.

The studies considered in this paper were carried out using aqueous solutions of 1 M LiCl, the salt being free of other alkali metals as impurities. The study with Na⁺ involved the use of 2 mM NaI in this solution. This concentration was chosen as being optimal for obtaining data in the limiting current region of the sodium wave, which occurs in practice in the same potential region as where lithium is reduced.

(i) Reduction of Li^+ from 1 M aqueous solutions

Significant impedance data were recorded at $-2.00 \ge E \ge -2.175$ V. Outside this potential range the d.c. current and the electrode admittance were inaccessible to precise measurement. The impedance data were transformed into the admittance components and were inspected, in the first instance, in plots of the real component, Y'_{el} , vs. the square root of frequency, $\omega^{\frac{1}{2}}$, at each potential studied. These plots were found to be curved, tending to become linear at $\omega^{\frac{1}{2}} < 80$ s^{- $\frac{1}{2}$}. Extrapolation of this linear portion to $\omega^{\frac{1}{2}} = 0$ yielded significantly positive intercepts at $E \ge -2.10$ V while at E < -2.10 V, positive intercepts of questionable significance could be found. This behaviour suggests that also in this case, two reactions proceed in parallel according to the equation⁵,

$$Y'_{e1} = \frac{\omega^{\frac{1}{2}}}{\sigma_1} \frac{p+1}{p^2 + 2p + 2} + \frac{1}{\theta_2}$$
(1)

where $p = \theta_1/\sigma_1 \omega^{-\frac{1}{2}}$, with p the irreversibility coefficient, θ_1 the charge transfer resistance and σ_1 the Warburg coefficient of the lithium reduction, and θ_2 is the charge transfer resistance of the parallel irreversible process. According to eqn. (1), the linearity of the Y'_{e1} vs. $\omega^{\frac{1}{2}}$ plots at low frequencies indicates that p is small, the slopes of these lines yielding directly values of σ_1 . Log σ_1 is plotted as a function of potential in Fig. 1. The straight line through the points has a slope of $-16.9 V^{-1}$ in agreement with the theoretical potential dependence of σ_1 in the case of a d.c. reversible electrode reaction. In this case, only ox present and $E \gg E_0$, the theoretical relationship is⁴,



Fig. 1. The Warburg coefficient as a function of potential for 1 M LiCl.

J. Electroanal. Chem., 34 (1972)

reduction of Li^+ and Na^+ on mercury

$$\sigma_{1} = \frac{RT}{n^{2}F^{2}c_{O}^{*}2^{\frac{1}{2}}D_{O}^{\frac{1}{2}}} \exp\left[\frac{nF}{RT}\left(E - E_{\frac{1}{2}}^{r}\right)\right]$$
(2)

where $E_{\frac{1}{2}}^{r}$ is the reversible half-wave potential. This corresponds to a theoretical value of -16.6 V^{-1} for the slope of the log σ_1 vs. E plot.

A significant irreversible contribution to the total admittance is again evidenced by the ordinate intercept. Its precise magnitude is subject to error as was found previously¹. Improved values of θ_2 are necessary before further analysis is possible. These were obtained by a combination of d.c. and a.c. methods. The current due to the Li⁺ reaction can be calculated rather precisely from σ_1 using ¹,

$$i_{\rm Li^+} = -\left(\frac{7}{6\pi t}\right)^{\frac{1}{2}} \frac{RT}{nF\sigma_1} \tag{3}$$

The total current, i_t as measured from a d.c. polarogram, is related to the irreversible reaction current, $i_{\rm H}$, and $i_{\rm Li^+}$ by,

$$i_{t} = i_{Li^{+}} + i_{H} \tag{4}$$

 θ_2 is related to the irreversible component $i_{\rm H}$ by¹,

$$\theta_2 = -\left(RT/nF\beta\right)i_{\rm H}^{-1} \tag{5}$$

where β is the cathodic transfer coefficient.

As i_{Li} + can be calculated from σ_{Li} + and i_t is known from the d.c. polarogram, i_H can be derived from eqn. (3). The three components of current are shown in Fig. 2.



Fig. 2. D.c. current vs. potential plots for 1 M LiCl at the dropping mercury electrode; (1) Total d.c. current passed by the electrode in the potential region studied, (2) current due to the reduction of lithium calcd. from the Warburg coefficient, (3) difference between (1) and (2), the current due to the irreversible reduction occurring during the reduction of lithium ions.

Fig. 3. Logarithmic plots of the current due to (×) lithium, (O) hydrogen as a function of potential.

1 M LiCl			2 mM Na ⁺		
-E/V	$\theta_2/\Omega \ cm^2$ a.c.	$\theta_2/\Omega \ cm^2$ d.c.	-E/V	$\theta_2/\Omega \ cm^2$ a.c.	$\frac{\theta_2/\Omega}{d.c.}$ cm ²
2.000	553	14000	1.925	5000	6400
2.025	400	7000	1.950	2000	3800
2.050	222	3200	1.975	1430	2180
2.075	143	1310	2.000	213	1040
2.100	32	648	2.025	115	514
2.125	20	262	2.050	111	408
2.140	9.6	174	2.075	59	262
2.150	9.1	132	2.100	36	194
2.160	5.6	86	2.125	_	143
2.175	3.6	62	2.150	—	118

TABLE 1

values of the charge transfer resistance, θ_2 , for the irreversible reaction in parallel with the cation reduction. Comparison of values derived from a.c. and d.c. measurements

There is, as observed previously¹, a significant contribution to the total current from the irreversible process. The logarithmic plot of the current contributions $i_{\rm H}$ and $i_{\rm Li^+}$ as a function of potential is shown in Fig. 3. The slope is 1/0.063 V⁻¹ which implies that $\beta n=0.95$, close to unity. It seems that in this case, as in the systems previously studied¹, the irreversible component results from the reaction of the amalgam with water or hydrogen ions.

Using eqn. (5) and the values of $i_{\rm H}$ shown in Fig. 3, more precise values of θ_2 were derived. These are shown in Table 1 where they are compared with the graphically extrapolated data derived from the maximum values of the ordinate intercept of the plots $Y'_{e1}vs.\omega^{\frac{1}{2}}$. As previously found, the extrapolated values do represent minimum values of θ_2 . The values of θ_2 derived from the d.c. data were then inserted in eqn. (1) and values of σ_1 and $p' = p/\omega^{\frac{1}{2}}$ were found by numerical computation¹. The calculated values of σ_1 agreed within experimental error with the data shown in Fig. 1. Significant values of p' (>3×10⁻³) were found. As indicated previously, these values can be checked by inspecting the imaginary part of the electrode admittance, given by⁵:

$$Y_{\rm el}^{\prime\prime} = \frac{\omega^{\frac{1}{2}}}{\sigma_1} \frac{1}{p^2 + 2p + 2} + \omega C \tag{6}$$

Equation (6) holds if it is assumed *a priori* that there is no coupling of double layer and faradaic parameters⁶. With the σ_1 values from Fig. 1, those values of p' were selected which gave frequency independent values of the double layer capacity C. Although these capacity values displayed considerable experimental error at the most cathodic potentials, the values of p' derived from this procedure agreed closely ($\pm 1 \times 10^{-3}$ for most potentials) with the values derived from the real part of the admittance.

As $E \gg E_0$, p' is given by the equation⁴:

$$p' = \left(\sqrt{2D_{\rm R}}/k_{\rm sh}^{\rm a}\right) \exp\left[-\alpha(nF/RT)\left(E - E_0\right)\right] \tag{7}$$

in which k_{sh}^{a} is the apparent rate constant. In accordance with this equation, a plot



Fig. 4. Plot of log p' as a function of electrode potential according to eqn. (7).

of log p' vs. E, presented in Fig. 4, is linear within the limits of error. From the slope of this plot the value $\alpha = 0.17 \pm 0.07$ is obtained. Extrapolation of this plot to $E = E_0$ would yield the apparent rate constant. However, only a value of E_{\pm} for the polarographic wave of Li⁺ in 0.1 M tetramethylammonium chloride is known⁷. If this potential is identified with E_0 (*i.e.* $D_0 = D_R$ and changes in activity coefficients are neglected), a value of $k_{\rm sh}^* = 0.14 \pm 0.07$ cm s⁻¹ may be calculated.

It is possible that k_{sh}^{a} contains a potential dependent term in which case both k_{sh}^{a} and α require correction for the influence of potential. This may be achieved on the basis of the Frumkin theory which relates k_{sh}^{a} to k_{sh}^{f} , the true formal rate constant, by⁸,

$$k_{\rm sh}^{\rm a} = k_{\rm sh}^{\rm f} \exp\left(-\alpha \phi_2 n F/RT\right) \tag{8}$$

where ϕ_2 is the potential of the outer Helmholtz plane. The transfer coefficient, as determined from Fig. 4, is the apparent anodic transfer coefficient α^a , related to the true transfer coefficient α by⁹,

$$\alpha^{\mathbf{a}} = \alpha + g \tag{9}$$

where

$$g = (RT/nF)(d \ln k_{\rm sb}^{\rm a}/dE)$$
(10)

The number of electrons transferred, n, is unity in this case.

In order to calculate the true formal rate constant and α , the values of ϕ_2 and $d\phi_2/dE$ in the potential region $-2.0 \ge E \ge -2.35$ V are required. The values of ϕ_2 are not directly available from tables in this extreme potential region and they were derived in the following manner. The capacity vs. potential function for 1 M LiCl was integrated from the point of zero charge $(-0.517 \text{ V vs. SCE})^{10}$ to the most cathodic

potential studied (-2.175 V), including the capacity data obtained in the potential region where Li⁺ is reduced. This yielded the electrode charge, $q^{\rm m}$, as a function of potential. If the absence of cation specific adsorption is assumed, ϕ_2 can be calculated directly from the Gouy--Chapman-Stern theory by¹¹,

$$q^{\rm m} = 11.72 \ c^{\frac{1}{2}} \sinh\left(19.46 \ \phi_2\right) \tag{11}$$

where the concentration c is in mol 1^{-1} , q^{m} is in $\mu C \text{ cm}^{-2}$ and ϕ_{2} is in volts. The value of ϕ_{2} (-98.7±1.5 mV) at the standard potential was found by extrapolation of plots q^{m} vs. E and ϕ_{2} vs. E to E_{0} . The mean probable errors from both extrapolation procedures were found to be similar. The slope, $d\phi_{2}/dE$, was found to be 0.042. Using eqns. (9) and (10), this results in a correction of 0.007 to the transfer coefficient, well within the probable experimental error in α . In this case α^{a} is the same as α . Using the value of ϕ_{2} at E_{0} together with the values of α and k_{sh}^{s} yields $k_{sh}^{f} = 0.07_{6} \pm 0.03_{7}$ cm s⁻¹.

The double layer capacity values, calculated from eqn. (6), are shown in Table 2. The maximum errors have been calculated by including a 1% error in the measured capacity value and a 1 Ω error in the solution resistance in the calculations.

TABLE 2

values of the double layer capacity in the presence of the Li^+ reduction

-E/V vs. SCE	$C/\mu F \ cm^{-2}$	Error in C: $\pm \Delta C/\mu F \ cm^{-2}$
2.000	23.1	0.1
2.025	24.1	0.2
2.050	24.9	0.3
2.075	25.8	0.4
2.100	26.2	0.5
2.125	26.7	0.7
2.140	28.4	1.0
2.150	28.9	1.5
2.160	29.1	3.0
2.175	29.6	6.0

(ii) The reduction of Na^+ at the dropping mercury electrode

This study is concerned with the reduction of Na⁺ from 2 mM solutions in 1 M aqueous LiCl supporting electrolyte. The impedance measurements, over the entire accessible faradaic range, were transformed into the admittance components. The admittance of the Na⁺ reaction, Y_{Na^+} , was separated from the total admittance, Y_{t} , using eqn. (12),

$$Y_{t} = Y_{Na^{+}} + Y_{Li^{+}}$$
(12)

where Y_{Li+} is the admittance of the reaction of the base electrolyte which was analysed in section 1 of this paper. After separation of Y_{Na+} from Y_t at each potential studied, the real and imaginary components of the electrode admittance of the Na⁺ reaction, Y'_{Na+} and Y''_{Na+} were treated in the usual way.

Plots of Y'_{Na+} vs. $\omega^{\frac{1}{2}}$, at each potential studied, yielded straight lines over the entire frequency range. This implies that the first term on the right-hand side of

REDUCTION OF Li⁺ AND Na⁺ ON MERCURY

eqn. (1) is reduced to $\omega^{\frac{1}{2}}/2\sigma_1$, due to the low values of p. Significant values of the intercept on the ordinate axis were recorded at E > -2.125 V.

The values of σ_1 , which now represent the Warburg coefficients of the Na⁺ reduction, are shown in Table 3. They evidently pass through a minimum. This behaviour is in accordance with the theory for a d.c. reversible reaction which gives for the potential dependence¹² of σ_1 ,

$$\sigma_1 = \sigma_1^{\rm m} \cosh^2 \frac{1}{2} \varphi_{\rm m} \tag{13}$$

where $\sigma_1^{\rm m}$ is the minimum value of σ_1 and $\varphi_{\rm m} = nF(E - E_{\rm m})/RT$. $E_{\rm m}$ is the potential at which the minimum value of σ_1 is attained. $E_{\rm m}$ is identical to $E_{\frac{1}{2}}^{\rm r}$, the reversible half-wave potential.

TABLE 3

comparison of theoretical and experimental values of σ_1 for 2 mM Na⁺ in 1 M LiCl supporting electrolyte

-E/V vs. SCE	$\frac{\sigma/\Omega \ cm^2 \ s^{-\frac{1}{2}}}{eqn. (12)}$	$\sigma/\Omega \ cm^2 \ s^{-\frac{1}{2}}$ exptl.
2.000	2290	2240
2.025	860	896
2.050	406	385
2.075	196	199
2.100	141	141
2.125	165	155

The experimental values are compared in Table 3 with the values predicted by eqn. (13), using a minimum value of $\sigma_1 = 138 \ \Omega \ cm^2 \ s^{-\frac{1}{2}}$. The data are in good agreement with theory.

As the reaction is entirely reversible, it is possible to calculate the theoretical d.c. polarogram, *i vs. E*, from the standard theoretical equation, which is for the d.c. reversible case⁷,

$$i_{\rm d}/i = 1 + \exp\left[(nF/RT)(E - E_{\star}^{\rm r})\right]$$
 (14)

In order to apply eqn. (14), values for the limiting current density, i_d and the half-wave potential, E_2^r , are necessary. The latter can be identified with the minimum potential of σ_1 , *i.e.* -2.107 ± 0.002 V vs. SCE. This agrees closely with the value given by Heyrovsky⁷, -2.104 V. Using the Ilkovič equation, the value of i_d may be calculated if a value can be assigned to D_0 , the diffusion coefficient of the sodium ion. This quantity may be derived from σ_1^n as follows¹²,

$$\sigma_1^{\rm m} = \frac{4RT}{n^2 F^2 2^{\frac{1}{2}} D_{\rm O}^{\frac{1}{2}} (c_{\rm O}^* + d^{\frac{1}{2}} c_{\rm R}^*)} \tag{15}$$

In this case $c_R^* = 0$ and the assumption that $D_0 = D_R$ frequently employed is unnecessary. This calculation yields $D_0 = 8 \times 10^{-6}$ cm² s⁻¹. Subsequent substitution of this value into the Ilkovič equation gave $i_d = 3.38 \times 10^{-4}$ A cm⁻².

The experimental d.c. polarograms were measured a number of times for the base electrolyte (1 M LiCl) and with the electroactive species at concentrations between

1 and 10 mM (Na⁺). Data anodic of $E_{\frac{1}{2}}$ could be obtained precisely, possible errors in the baseline making the procedure inaccurate at the lowest current densities. Data cathodic of $E_{\frac{1}{2}}$ could only be acquired with the greatest difficulty as the determination of a difference < 15% of the total current ($i_{\text{Li}} + i_{\text{Na}+}$) measured was involved. As the current–voltage characteristic is very steep in this potential region, the possible errors in the original measurement may be as high as 5%. In order to obtain sensible limiting current values, the mean of the data from 10 polarograms was used, resulting in a value of $i'_{\text{d}} \sim 5.8 \times 10^{-4} \text{ A cm}^{-2}$.

The experimental d.c. polarogram for the 2 mM Na⁺ solution and the theoretical polarogram calculated from eqn. (14) using i_d derived from σ_1^m , are shown in Fig. 5. The difference between these two current-potential characteristics represents the current contribution due to the irreversible reaction occurring in parallel with the Na⁺ reduction. The dependence of the irreversible current on the presence of the Na⁺ reduction is immediately obvious, the shapes of the three curves being similar.



Fig. 5. D.c. current vs. potential plots for $2 \text{ m}M \text{ Na}^+$ in a supporting electrolyte of 1 M LiCl after separation of the current contribution due to Li⁺. (1) Experimentally observed current due to $2 \text{ m}M \text{ Na}^+$, (2) theoretical polarogram caled. from eqns. (12)–(15), (3) current due to the irreversible reaction in parallel with the Na⁺ reduction.

The values of θ_2 calculated from eqn. (5), using the values of i_H in Fig. 5, are compared in Table 1 with the data derived from the mixed current analysis according to eqn. (1). As in previous studies, the θ_2 values directly derived from the a.c. data appear to be minimum values.

DISCUSSION

The apparent rate constant for the reduction of Li^+ (0.14 cm s⁻¹) is smaller than that for Na⁺ and K⁺ (>3.4 cm s⁻¹). The limiting rate constant for Na⁺ and K⁺

was estimated by assuming that $p' = 5 \times 10^{-4}$ at $(E - E_0) = 0.13$ V, that α is arbitrarily set equal to the value found for Li⁺ (0.17) and $\dot{D}_R = 8 \times 10^{-6}$ cm² s⁻¹. These values were then substituted into eqn. (7). The differences between the formal rate constants of these systems is even larger. The potential of the outer Helmholtz plane at E_0 for K⁺ and Na⁺ is considerably less than it is for Li⁺. This results in a smaller Frumkin correction for Na⁺ and K⁺. A different reduction rate for Li⁺ might be correlated with the unusual chemical characteristics of the ion as exemplified by the high degree of hydration, a direct result of the small ionic radius.

It is possible to compare the values of the double layer capacity found in 1 Msolutions of the different cations. The rise in capacity observed in the previous study with Na^+ and K^+ , is not evident from the data in Table 2 in spite of the fact that the faradaic regions are comparable, the d.c. current for the Li⁺ reaction at -2.175 V being the same as the d.c. current observed at -1.990 V in the K⁺ system. It is arguable that the rise in capacity may occur at still more cathodic potentials. In view of the difference between K⁺ and Na⁺, and Li⁺, the cathodic rise may be usefully correlated with the degree of cationic specific adsorption. The degree of specific adsorption might be expected to be in the order $K^+ > Na^+ > Li^+$. The only inorganic cation which has been studied¹³ systematically in the cathodic potential region is Cs⁺. Significant specific adsorption was found over a wide range of cathodic potentials. Gierst et al.¹⁴ suggest that if Li⁺ is assumed to be non-adsorbed, K⁺ and Na⁺ display significant specific adsorption, although too little to be detected by procedures employing the Gouy-Chapman-Stern theory. The lack of rise in capacity in 1 M LiCl, when compared with the similar sodium and potassium systems, supports the evidence as presented by Gierst. A more precise estimate of the degree of specific adsorption of these ions in the faradaic region is precluded by the lack of precision in the data.

The presence of the irreversible accompanying reaction has two important consequences. Firstly, as argued in the previous paper¹, deviations from the Nernst potential will be apparent during potentiometric measurements of the alkali metal/ alkali ion electrode. For the Li⁺ system, this deviation will be 21 mV. Secondly, the apparent diffusion coefficient, D_0 , as derived from the limiting current of the experimental d.c. polarogram of Na⁺, is almost 3 times too high. Recent d.c. polarographic investigations by Broadhead and Elving support this observation¹⁵. From their data it can be inferred that the diffusion coefficient of Na⁺ in 0.1 *M* tetraethylammonium perchlorate in water is 2.8×10^{-5} cm² s⁻¹. This is indeed an unusually high value, being about three times higher than the value derived in the present work from a.c. measurements. This indicates that, also in tetraethylammonium perchlorate as supporting electrolyte, the accompanying irreversible reaction contributes significantly to the total current.

The suggestion in the previous paper¹ that the amalgam catalyses the water reduction is confirmed by the studies presented in this paper. The results pertinent to this argument may be summarised as follows. In the first place, no water reduction occurs before the onset of the Li⁺ wave. Secondly, as in the previous study, there is a potential independent ratio between $i_{\rm H}^{\rm Li^+}$ and $i_{\rm Li^+}$. Finally, the shape of the Na⁺ polarogram in 2 mM concentration is the same as the shape of the $i_{\rm H}$ polarogram (cf. Fig. 5) although rather large errors are inherent to the analysis.

The correlation between the different potential regions over which the hydrogen current is observed and the different half-wave potentials of the cations has already been

presented as evidence for a cation dependence of the hydrogen current¹. The potential independent ratio $i_{\text{Li}} + /i_{\text{H}}$ is 0.82 compared to similar ratios for sodium and potassium which can be derived from the previous paper and can be shown to be $i_{\text{Na}} + /i_{\text{H}} = 1.0$ and $i_{\text{K}} + /i_{\text{H}} = 1.34$. Another way of comparing the data is in terms of the rate constant, k^{H} , defined by the equation¹,

$$i_{\rm H} = nF k^{\rm H} c_{\rm H_2O} c_{\rm alkali} \tag{16}$$

where $c_{H_{2O}}$ and c_{alkali} are the surface concentrations of water (or protons) and amalgam respectively. As c_{alkali} is directly proportional to i_{alkali} , the current due to the alkali metal, the ratio between $kc_{H_{2O}}$ for the different alkali metals is readily calculated. This calculation yields $k_{H^+}^{H}: k_{Na^+}^{H}: k_{L_{1}^+}^{H}$ as 1:1.3:1.6, assuming the water to be in excess.

The studies with mM Na⁺ are less precise and cannot be subjected to this rigorous analysis. The ratio $i_{\rm H}/i_{\rm Na^+}$ varies widely over the potential range studied (2.4–0.76). The most precise values probably lie in the range, -2.050 > E > -2.125 V from which data an average value of unity might be derived.

It is worthwhile, nevertheless, to note that after subtraction of the admittance due to the Li^+ reduction (including the contribution of the lithium catalysed water reduction to this admittance), there remains an admittance, in the presence of 2 mM Na⁺, which can be split up into a reversible sodium reduction process (the potential dependence of which is in agreement with theory) and a water reduction process (catalysed by the alkali metal amalgam). The two reactions, Na⁺ and Li⁺ seem entirely independent.

Two general conclusions may be drawn from this study. The evolution of hydrogen occurs irrespective of the concentration of the alkali metal ions in the bulk solution. Secondly, the direct relationship between amalgam concentration and hydrogen evolution current has been confirmed.

ACKNOWLEDGEMENTS

The award of a European postdoctoral fellowship to one of us (R.M.R.) by the Royal Society is gratefully acknowledged. This investigation was also supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

SUMMARY

The reduction of Li⁺ ions in 1 *M* concentration and the reduction of Na⁺ ions in m*M* concentration in aqueous solution, has been studied at the dropping mercury electrode, using d.c. polarography and electrode impedance measurements, as a function of frequency and electrode potential. The reduction of Li⁺ was found to be quasireversible ($k_{sh}^{f}=0.08\pm0.04$ cm s⁻¹). The reduction process was accompanied by an irreversible secondary process as was found previously for K⁺ and Na⁺ reductions. This is attributed to the reaction of the alkali metal amalgam with water. The error in potentiometric measurements of the standard potential of the lithium/lithium ion couple has been calculated (21 mV). The reversibility of the Na⁺ reaction was confirmed by the measurements in m*M* concentration. The presence of the irreversible reaction due to water reduction was detected over the entire polarographic reduction

range of the Na⁺ ion. This irreversible reaction was found to be in agreement with the theory developed for the process in the presence of 1 M alkali metal ions.

REFERENCES

- 1 R. M. REEVES, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, J. Electroanal. Chem., 34 (1972) 55.
- 2 H. IMAI AND P. DELAHAY, J. Phys. Chem., 66 (1962) 1683.
- 3 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, Rec. Trav. Chim., 83 (1964) 983.
- 4 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, Rec. Trav. Chim., 82 (1963) 525.
- 5 B. G. DEKKER, M. SLUYTERS-REHBACH AND J. H. SLUYTERS, J. Electroanal. Chem., 23 (1969) 9.
- 6 P. DELAHAY, J. Phys. Chem., 70 (1966) 2373.
- 7 J. HEYROVSKY, Principles of Polarography, Academic Press, New York, 1966.
- 8 A. N. FRUMKIN, Z. Phys. Chem., 164 (1933) 121.
- 9 M. SLUYTERS-REHBACH, B. TIMMER AND J. H. SLUYTERS, Z. Phys. Chem. N. F., 52 (1967) 89.
- 10 R. M. REEVES, unpublished data.
- 11 D. MOHILNER, Electroanalytical Chemistry, Vol. 1, Marcel Dekker, New York, 1966, p. 241.
- 12 M. SLUYTERS-REHBACH, Thesis, Utrecht, 1963.
- 13 R. PARSONS AND A. STOCKTON, J. Electroanal. Chem., 15 (1970) App. 10.
- 14 L. GIERST, E. NICOLAS AND L. TYTGAT-VANDENBERGEN, Croat. Chem. Acta, 42 (1970) 117.
- 15 J. BROADHEAD AND P. J. ELVING, J. Electrochem. Soc., 118 (1971) 63.