Determination of the double-layer capacity of porous nickel in KOH in the presence of faradaic current

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Experimental and analytical techniques to determine the double-layer capacity of porous electrodes in the presence of faradaic effects are discussed. A triangular voltage sweep method was used with commercially available porous nickel plaque electrodes in KOH. No elaborate purification pretreatments were needed. A minimum double-layer capacity of about $28\,\mu\text{F cm}^2$ was determined at -0.40 V versus Hg/HgO which is close to the pzc reported for nickel. Overall the results agreed well with literature values for solid nickel.

1. Introduction

Double-layer capacity (DLC) measurements provide a useful method of studying porous electrode systems. They are an effective way of determining the wetted area available for electrochemical reaction which is not always the same as the BET area [1]. The DLC of the electrode is a function of the nature of the metallic phase, electrode potential, composition of the solution, and temperature. In addition, porous electrodes may give rise to distributed reactions [2] which complicate analyses of the data. The measurements also reflect the presence of pseudo-capacity effects associated with impurities or other adsorbable species present at the electrode surface or in solution [3]. A modified triangular voltage sweep (TVS) method which has been described in earlier work [1–4] is ideally suited for porous electrode systems because faradaic and distributed capacity effects can be systematically eliminated, either experimentally or analytically. This paper will discuss two methods of eliminating or at least minimizing faradaic effects. A porous nickel electrode was used in 8 M KOH, and the DLC was determined as a function of temperature and potential.

2. Experimental

Details of the electrochemical cell, the Teflon electrode holder and instrumentation are given elsewhere [3]. The porous nickel electrodes were punched from a sheet of commercially available sintered battery plaque; they were disk-shaped, had a geometric area of $9.6\,\text{cm}^2$ and an internal area of $705\,\text{cm}^2$ determined from the BET surface area where nitrogen was the adsorbate. The cell and a Hg/HgO reference electrode with Luggin capillary were mounted in a constant temperature cabinet; triangular voltage sweeps were made at four temperatures between 22 and $-46°\text{C} \pm 0.5°\text{C}$. Measurements were performed with a potentiostat and a signal generator; a two-pen strip chart recorder plotted potential-time and current-time traces from which capacities as a function of time were calculated from

$$C = \frac{i}{k} \tag{1}$$

where C is capacity (F), i is current (mA) and k is sweep rate (mV s^{-1}). No precautions were taken to prepurify the solutions other than to use reagent grade chemicals and distilled water.

3. Results and discussion

3.1. *Room temperature data*

Figs. 1 and 2 show current versus time traces for a porous nickel electrode in 8 M KOH subjected to single triangular voltage sweeps. Each sweep begins at a different potential between 0 and -0.70 V
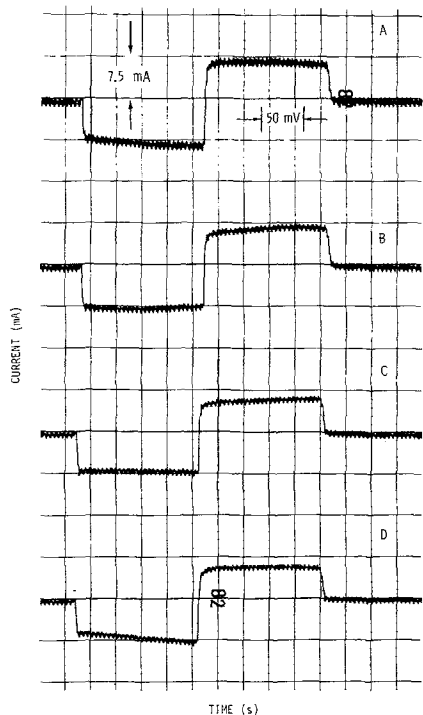
Fig. 1. Single triangular voltage sweeps at 21° C using a sweep rate of 299 mV s^{-1}. The sweeps have a voltage excursion of 140 mV and a different starting potential beginning at A: 0 V versus Hg/HgO; B: $-0\cdot10$ V; C: $-0\cdot20$ V; D: $-0\cdot30$ V.
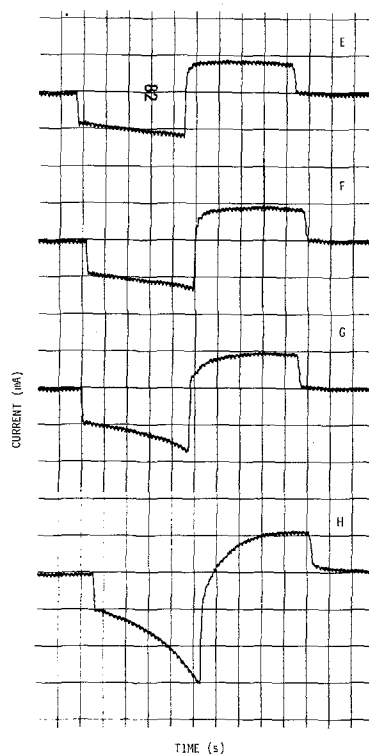

Fig. 2. Continuation of Fig. 1. E: $-0\cdot40$ V; F: $-0\cdot50$ V; G: $-0\cdot60$ V; H: $-0\cdot70$ V.

versus Hg/HgO, covers a voltage range of 140 mV to keep transient faradaic current not too large compared to capacitative current and has the same sweep rate of 299 mV s^{-1}. Distributed capacity effects arising from resistance of the electrolyte within the pores of the electrode and discussed in earlier work [2, 4] were minimized experimentally as evidenced by the lack of curvature at the start of the sweep and at sweep reversal. Over the range of potentials selected, the shapes of the current-time curves change with potential. This can be seen more clearly by taking the current at some potential just prior to sweep reversal and plotting the current versus potential (see curve A, Fig. 3); the right ordinate of Fig. 3 shows C*, the apparent capacity per BET area of the electrode. At about $-0\cdot25$ V, a capacity minimum of 32 μF cm^{-2} is observed. As the potential becomes more cathodic, the current increases rapidly, especially in the vicinity of $-0\cdot80$ V (also seen in Fig. 2H). This is very close to the potential at which the reduction of nickel hydroxide to nickel metal occurs according to Latimer [5]
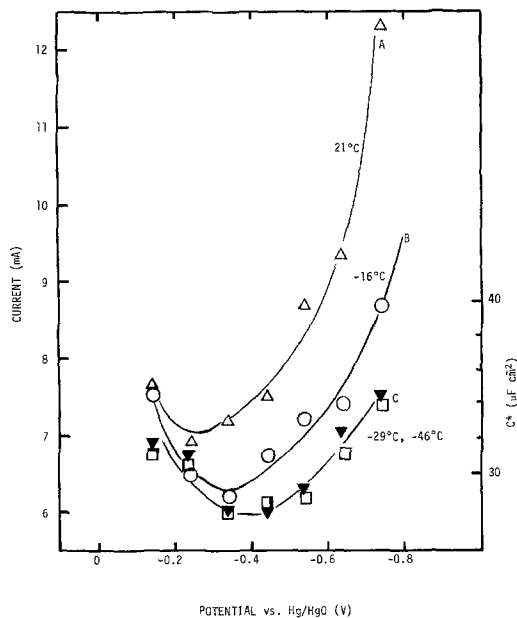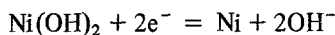

Fig. 3. Potential versus current (left ordinate) or apparent capacity per BET area (right ordinate) as a function of temperature.

$$Ni(OH)_2 + 2e^- = Ni + 2OH^-$$

which has a standard reduction potential, $E_{SHE}^0 = -0.72$ V (-0.82 V versus Hg/HgO). Therefore, the total current measured, i_t, is the sum of at least two effects

$$i_t = i_{DL} + i_F \qquad (2)$$

where i_{DL} is the current due to the double-layer and i_F is faradaic current. Therefore, to obtain the capacitative current, i_{DL}, the faradaic current must be eliminated or at least minimized.

3.2. Low temperature effects

Sweeps similar to those shown in Fig. 1 and 2, but at -16, -29 and $-46°C$ were obtained. The total current, i_t, was plotted as a function of potential in Fig. 3. As temperature is lowered, a decrease in the apparent capacity of the electrode occurs. From 21 to $-29°C$, the value of the minimum capacity decreases from 32 to $27.5 \, \mu F \, cm^{-2}$, a decrease of $0.9 \, \mu F \, cm^{-2}$ per $10°C$ change in temperature; below $-29°C$, the decrease in capacity is negligible. McCallum et al. [6] found that the capacitance minimum for a solid nickel foil electrode in 7.4 M KOH decreased about $1.5 \, \mu F \, cm^{-2}$ for an $8.5°C$ change in temperature from 55 to $25°C$.

3.3. Faradaic current corrections

In previous work [2, 4] it was shown that when distributed reactions are negligible and faradaic currents are significant, but not too large compared to the double-layer capacity, it is possible to estimate the DLC of the electrode at the reversal point of the sweep (see Fig. 4) from

$$C_{DL} = i_r/k$$
$$= (i_1 + i_2)/2k. \qquad (3)$$

For example, consider Fig. 1A where $i_r = (i_1 + i_2)/2 = 4.6$ divisions $= 6.9$ mA. Taking $k = 299 \, mV \, s^{-1}$ and the BET area of $705 \, cm^2$, the DLC corrected for faradaic current using Equation 3 has a value of $32.7 \, \mu F \, cm^{-2}$. Similar calculations were made for the other traces shown in Fig. 1 and 2, and the values are plotted in Fig. 5. Capacities calculated from the initial current step at the start of the sweep (i_s, Fig. 4) are shown in Fig. 5. The
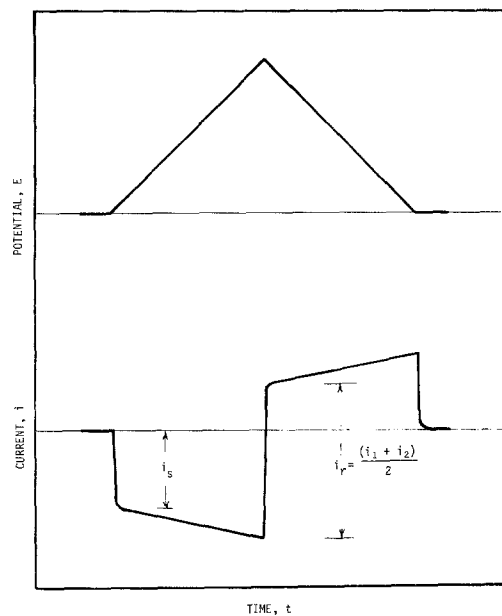

Fig. 4. Illustration of $i - t$ plot for a single triangular voltage sweep in the presence of faradaic current.
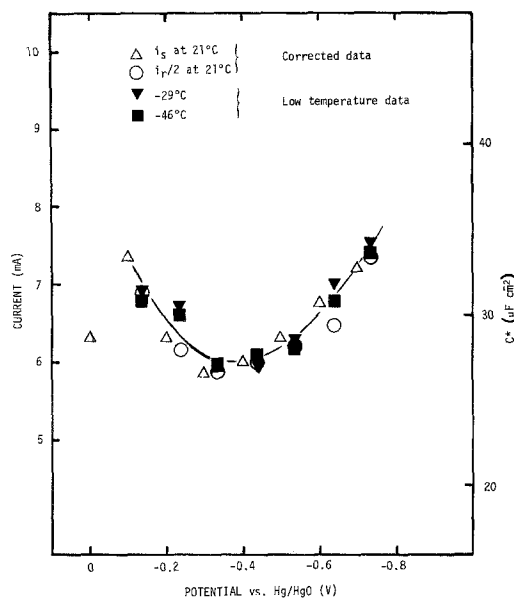

Fig. 5. Potential versus current (left ordinate) or apparent capacity per BET area (right ordinate). $\triangle$ i_s values obtained at $21°C$; $\circ$ i_r values obtained at $21°C$; $\blacktriangle$ $-29°C$ data; $\blacksquare$ $-46°C$ data.

low temperature data from Fig. 3C are also included for comparison. The agreement between the low temperature data and the $21°C$ data that

have been corrected for faradaic effects is good. The double-layer capacities are also in good agreement with literature values for solid nickel in 1 M Na_2SO_4 [7], 1 M K_2SO_4 [8] and 1 M KNO_3 [8]. McCallum *et al.* [6] found that the capacity minimum for nickel foil in 7·4 M KOH at room temperature was 31 $\mu F\,cm^{-2}$ at −0·70 V versus SCE (−0·46 versus Hg/HgO). Furthermore, the voltage of the capacity minimum determined in this study is close to the pzc value of −0·27 to −0·33 V versus NHE reported for solid nickel [9].

4. Summary and conclusions

A triangular voltage sweep technique using short voltage excursions over a wide range of potentials was used to determine the double-layer capacity of porous nickel in 8 M KOH as a function of temperature. At 21°C the capacity reflected a contribution from some faradaic process, most likely due to the reaction

$$Ni(OH)_2 + 2e^- = Ni + 2OH^-.$$
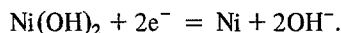
As the temperature was decreased, faradaic current was suppressed in the potential range of 0 to −0·70 V versus Hg/HgO; below −29°C, no further reduction in faradaic current was noted. The low temperature results coincided very well with values determined from the 21°C data that had been corrected for faradaic current; the corrected

capacities were determined from the initial current step at the start of the sweep and at the point of sweep reversal.

The double-layer capacity of the nickel electrode varied with potential and had a minimum value of about 28 $\mu F\,cm^{-1}$ at −0·40 V versus Hg/HgO. The capacities were found to be in good agreement with literature values for solid nickel. Also, the capacity minimum occurred in the vicinity of the pzc reported for solid nickel. This paper shows effective ways of determining the double-layer capacity of a porous electrode in the presence of faradaic current.

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