

OXIDATION OF HYDROGEN ON A POROUS NICKEL ELECTRODE*

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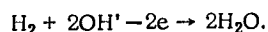
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Porous electrodes are of considerable interest as a means of accelerating slow electrochemical processes. Ways of using porous applications efficiently are fairly extensive [1-7]. Their main applications are for electrolysis with evolution of gases, electrosynthesis, various depolarizing processes using gaseous and liquid substances, and as chemical sources of current (especially fuel cells).

The operation of these electrodes is governed to a large extent by macrokinetic factors associated with transfer of the substance and the passage of electric current through the electrode pores. For example, in gas diffusion electrodes in fuel cells the over-all rate of the process depends on the effective permeability of the gas and liquid phases in the electrode pores, dissolution and diffusion of the active substance through the film of liquid covering the electrode pores, and the rate of the electrochemical process itself. Superposition of these factors seriously complicates any study or analysis of porous electrode processes.

This paper gives the results of an investigation into oxidation of hydrogen on a porous nickel electrode in an alkaline medium:



This process takes place on the negative electrode in a hydrogen-oxygen fuel cell.

Such an investigation involves numerous difficulties. Oxidation of hydrogen on nickel is a very slow process; therefore, a sufficiently high degree of purity must be ensured when carrying out the experiment. Account must be taken of the fact that the intensity of the process is not uniform over the thickness of the porous electrode. As a result of the poor solubility of hydrogen in an electrolyte, the concentration polarization has a considerable effect, even at low currents.

For the investigation of hydrogen oxidation kinetics on nickel we used a method based on an analysis of the phenomena occurring when an electrode is charged with a constant current. In this way we were able to reduce the concentration effects considerably and determine the area of the electrode's inner surface. Similar methods based on a study of the transient phenomena caused by switching the current on and off are widely used when examining smooth electrodes [8-11]. The adoption of these methods for studying porous electrodes was justified in [7, 12-14]. In the present paper we employed mainly the results of calculations in [14].

EXPERIMENTAL

Figure 1a gives a diagram of the electrolytic cell. The test electrode, a disc of 2 cm diameter, was secured in a fluoroplastic box (1), designed to simplify electrode exchange (Fig. 1b).

Provision was made for drawing in fresh electrolyte via the electrode. When a vacuum was established in the cylinder (a, 2), valve (3) closed and the electrolyte was drawn into the cylinder via the electrode. When hydrogen was fed-in under pressure, the electrolyte was expelled from the cylinder, through the valve and into the cell. Current reached the electrode via nickel wire passed through the cylinder and box and terminating in sprung contacts. The platinum polarizing electrode (4) was separated from the main electrolyte by a glass diaphragm (5). To saturate the electrolyte, the hydrogen was introduced at a pressure of ~0.3 atm through fine-pored platinum filter (6) (glass filters fail rapidly in alkaline solution). Pure hydrogen was provided by an electrolyzer with a porous valve-type cathode [15].

* Communication 1.

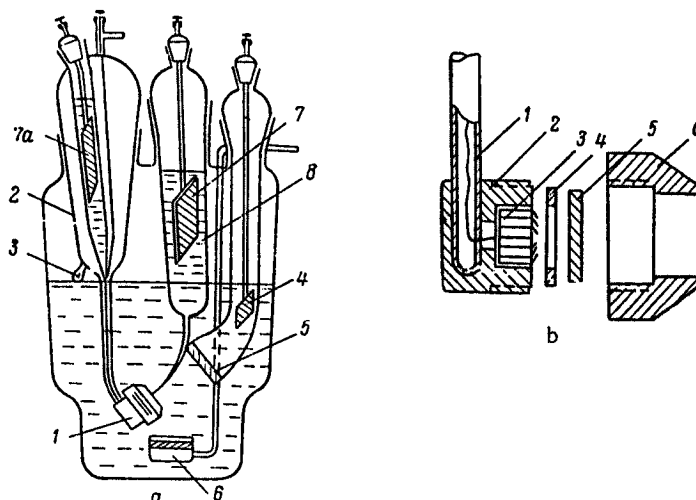


Fig. 1. Electrolytic cell. a) General view (described in text), b) box.
b: 1) Glass tube, 2) body, 3) sprung conductor, 4) liner, 5) electrode, 6) lid.

The reference electrode was a nickel oxide electrode (7) placed in a tube terminating in an electrolytic key (8). To measure the potential of the rear face of the electrode, a similar reference electrode (7a) was inserted in cylinder (2). During work the reference electrode potential was almost constant, being about 1.34 V in relation to the hydrogen electrode in the 1N alkali. The reference electrode's potential was checked periodically against the hydrogen electrode; thermostat control of the cell was within limits of $\pm 0.5^\circ$.

The electrolyte was 1N NaOH solution, prepared from pure alkali obtained by decomposing a sodium amalgam. The solution was purified by cathodic polarization for 18-24 h after preliminary hydrogen-blowing of the air dissolved in the electrolyte. The cathode used for treating the electrolyte was an auxiliary nickel electrode; the electrolyte was continuously saturated with hydrogen during measurements.

Figure 2 shows the arrangement for recording porous electrode charging curves. The current source in the polarizing circuit was a 40 V battery, variable resistances being used to regulate the polarizing current within limits of 0.1 to 500 mA. Current strength was checked by a milliammeter which could be cut out during curve recording. Switch (n2) served for reversing the polarizing current.

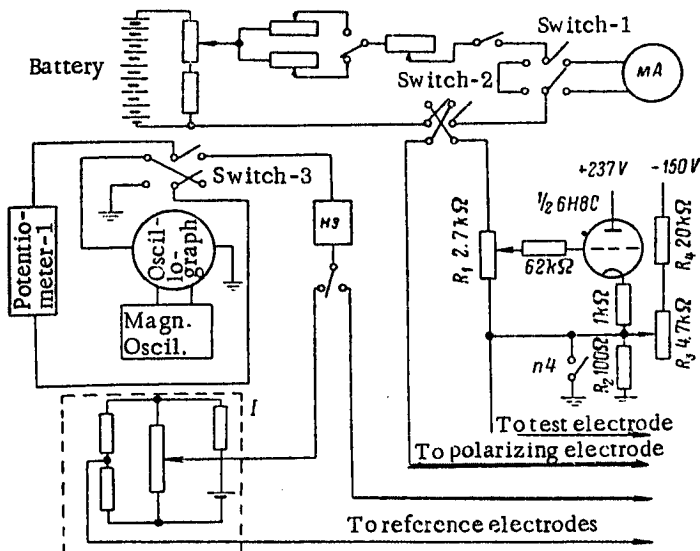


Fig. 2. Set-up for recording charging curves.

Provision was made for compensating the ohm voltage drop in the nickel conductor, the contact, the electrode and the electrolyte between the electrode and the tip of the electrolytic key. A simple electronic principal was employed, working on a tube 6H8. The constant component of the potential difference of the test and reference electrodes was compensated by a counter-switched Weston cell and a potentiometer.

The reference electrode (7 and 7a, Fig. 1a) potentials may differ slightly; to match them exactly, use was made of an auxiliary circuit (I, Fig. 2) on a bridge principle. An oscillograph served as the zero instrument and also for visual tracking of the charging curves and amplifying the direct current. From the output stage of the oscillograph's vertical amplifier, the current was passed through an additional resistance to the vibrator of the magnetic oscillograph. The oscillograms were recorded by highspped filming (2 to 250 mm/sec); their scale along the potential axis being adjusted by switching in a known potential difference from the potentiometer. Maximum sensitivity on the film was 1.7 mm/mV. The time scaling of the oscillograms was effected by a time marker; the whole circuit was screened by an earthed screen.

Normally the electrode did not acquire a potential corresponding to that of an equilibrium hydrogen electrode immediately, it was immersed in the hydrogen-saturated electrolyte, evidently because the surface of the nickel is oxidized by contact with the air before immersion [16]. To obtain a steady value for the equilibrium potential, it is sufficient to subject the test electrode to cathodic polarization with a current of ~ 2 mA for 10-15 min (the electrolyte being passed intermittently through the electrode). When the current was cut off, the equilibrium hydrogen potential was established after a few minutes and then remained constant.

After this initial procedure, the charging curves were recorded. The charging current was selected to give an electrode potential shift of not more than 20-30 mV. After each current switching, fresh electrolyte was passed through the electrode to exclude concentration changes in the pores. The oscillograms, recorded either with a photomagnifier or epidiascope, were transferred to millimeter paper for further analysis.

EXPERIMENTAL

Figure 3 gives typical charging curves for porous electrodes at different currents. In the initial period after switching the current in, the electricity is consumed in charging the double layer. As the electrode potential rises, so does the Faraday component of the current, whereas the capacitive component decreases accordingly. The steepness of the charging curve becomes less marked at this stage. With weak currents, steady polarization (curve 1) sets in after a little while. With high polarizing currents, concentration phenomena become more marked.

Initially, concentration polarization increases linearly with time (sectors b in curves 2, 3); the limiting value of chemical polarization can therefore be found by extrapolation. If the polarizing current is fairly small, and the consumption of active substance in the electrode pores can be compensated by diffusion from the surrounding electrolyte, steady polarization will gradually be achieved (sector c, curve 2). Conversely, with powerful currents steady polarization is absent, so that when the reserve of active substance in the electrode pores is exhausted its polarization increases markedly (sector c, curve 3).

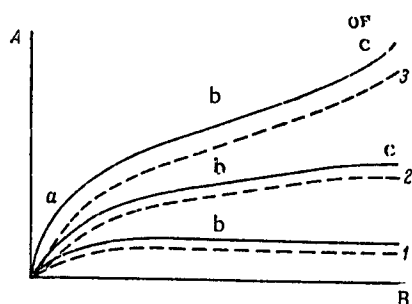


Fig. 3. Porous electrode charging curve shapes at different currents ($I_3 > I_2 > I_1$). A) Polarization, η (mV); B) time, t (secs). Continuous lines: polarization of exterior of electrode. Broken lines: rear face of electrode.

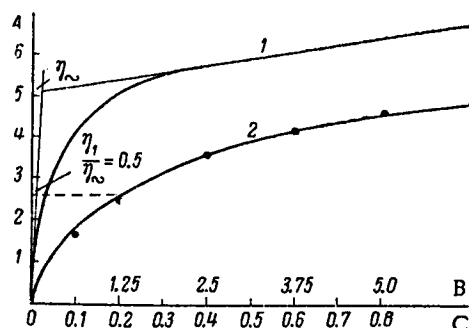


Fig. 4. Example of charging curve for a porous electrode with current 0.3 mA/cm^2 . A) Polarization, η (mV); B) time for curve 1 (sec.); C) time for curve 2 (sec.). Recording speed (mm/sec): 1, 4; 2, 25. Dots: calculated values.

The charging curves for the rear face of the electrode differ from those for its exterior (dotted lines in Fig. 3). Initially, after switching in the current and while there is little change in the exterior surface's potential, the charging wave does not penetrate to the electrode rear face; therefore, at the latter there is a slight lag of the potential change (governed by the thickness of the electrode). Polarization of the rear face of the electrode is less than of its exterior.

We used the results of calculations in [14] to analyze the experimental charging curves. Below we give an example of the calculation of the electrode characteristics from the charging curves.

By way of example we used an electrode pressed from nickel carbonyl (mean particle size 6μ), subsequently fired in hydrogen. It was a disc of diameter 1.7 cm and thickness 0.3 cm; porosity of the testpiece was 62.5%.

Figure 4 shows the charging curve of this electrode, with current $I = 0.3 \text{ mA/cm}^2$, temperature 60° . The charging curve was recorded twice: first (curve 1) at a film speed of 4 mm/sec. Here, the rectilinear sector of the curve was clearly visible, caused by increasing concentration polarization. In the second case, we recorded the initial sector of the charging curve (curve 2) at a film speed of 25 mm/sec. Steady kinetic polarization of the electrode (η_∞), found by extrapolating the rectilinear sector of the charging curve, was 5.1 mV. These data provide the dimensionless, derived thickness of the electrode (δ), equal to the ratio of its actual thickness (l) to its characteristic thickness (x_e) [14]. For this we calculate as follows:

$$\frac{I\rho l}{\eta_\infty} = \frac{0.3 \cdot 10^{-3} \cdot 10.7 \cdot 0.3}{5.1 \cdot 10^{-3}} = 0.19$$

(where ρ is the effective resistance of the electrolyte in the electrode pores; at 60° $\rho = 10.7 \text{ ohm} \cdot \text{cm}$). This ratio is equal to the product of $\delta \cdot \text{th } \delta$. With low δ values we may consider $\delta \approx \text{th } \delta$, so for this case we obtain $\delta = \sqrt{0.19} = 0.435$.

The derived thickness can also be found from the ratio of polarization to rear-face polarization on the porous electrode [14]:

$$\frac{\eta_{\text{outer}}}{\eta_{\text{rear}}} = \text{ch } \delta.$$

In this case, $\eta_{\text{rear}} = 4.65 \text{ mV}$. Hence, $\text{ch } \delta = 1.094$ and $\delta = 0.43$; this is very near the value obtained above.

Employing the value found for δ , we calculated x_e , the effective depth of penetration of the process (or characteristic thickness of the electrode):

$$x_e = \frac{l}{\delta} = \frac{0.3}{0.435} = 0.69 \text{ cm}.$$

Then we found the characteristic time τ . For this, we find on the charging curve (curve 2, Fig. 4) the time t_1 , when the polarization of the electrode is half the steady value: $(\eta_t)/\eta_\infty = 0.5$. In the given case $t_1 = 0.20 \text{ sec}$. From the derived curve in [14], the ratio η_t/η_∞ , equal to 0.5 where $\delta = 0.435$, corresponds to the derived time $\theta = (t_1)/\tau = 0.64$. Hence, we find $\tau = (0.20)/0.64 = 0.313 \text{ sec}$. Proximate values are obtained at other η_t/η_∞ ratios.

Knowing τ , we find the exchange current:

$$i_0 = \frac{1}{2} \frac{bC'}{\tau},$$

where b is a constant equal here to 0.057 V; C' is the capacitance of the double layer per cm^2 surface of the porous electrode.

Assuming C' to be $20 \mu\text{F/cm}^2$,

$$i_0 = \frac{1}{2} \cdot \frac{0.057 \cdot 20 \cdot 10^{-6}}{0.313} = 1.83 \cdot 10^{-6} \text{ A/cm}^2.$$

The electrode capacitance is calculated by this formula:

$$C = \frac{\tau}{x_e^2 \rho} = \frac{0.313}{0.69^2 \cdot 10.7} = 0.0608 \text{ F/cm}^3 = 60800 \mu\text{F/cm}^3.$$

Then we find the specific surface of the electrode:

$$S = \frac{C}{C'} = \frac{60800}{20} = 3040 \text{ cm}^2/\text{cm}^3.$$

Figure 4 also gives points calculated by the electrode characteristics found here; there is satisfactory agreement between these calculated points and the experimental curve.

The charging curves can be used to calculate the hydrogen concentration in the electrolyte occupying the pore space of the electrode. The hydrogen concentration was found by this formula [14]:

$$c_0 = \frac{RTSt_0}{(nF)^2bg \left(\frac{\partial \Delta \eta}{\eta \Delta t} \right)} \cdot \left[1 + \frac{2\delta}{\text{sh}(2\delta)} \right],$$

where g is volumetric porosity, $(\partial \Delta \eta)/\partial t$ is the slope of the straight sector of the charging curve (Fig. 3, sector b).

In this case $(\partial \Delta \eta)/\eta \partial t = 0.0502 \text{ sec}^{-1}$ and $g = 0.625$. Hence,

$$c_0 = \frac{8.3 \cdot 333 \cdot 1.83 \cdot 10^{-6} \cdot 3040}{0.057 (2 \cdot 96500)^2 \cdot 0.625 \cdot 0.0502} \left[1 + \frac{2 \cdot 0.435}{\text{sh}(2 \cdot 0.435)} \right],$$

$$c_0 = 0.484 \cdot 10^{-6} \text{ mole/cm}^3.$$

We found no reference data on the solubility of hydrogen in 1.0 N alkali at 60°. Hydrogen solubility in a 1.0 N alkali solution at 25° is virtually the same as in water. In water at 60°, at atmospheric pressure, hydrogen solubility at 60° is $0.56 \cdot 10^{-6} \text{ mole/cm}^3$.

Hydrogen oxidation on a porous nickel electrode was investigated at 30, 45, 60, 75, and 90°. The exchange current within these limits varied from $0.7 \cdot 10^{-6} \text{ A/cm}^2$ at 30° to $3.8 \cdot 10^{-6} \text{ A/cm}^2$ at 90°. The activation energy calculated by the temperature function of the exchange current was 6.6 kcal/mole. These data are fairly close to those of Bockris and Potter [17] for hydrogen emission on smooth nickel.

SUMMARY

The oxidation kinetics of alkali-dissolved hydrogen on a porous nickel electrode were investigated. Use was made of the porous electrode charging curves method which greatly reduced the effect of concentration phenomena and provided data on the inner surface area of the electrode. The specific electrode surface, the exchange current and activation energy of the process were determined. For porous nickel these values are similar to those obtained for smooth nickel.

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