# POLARIZATION CHARACTERISTICS OF CIRCULATING POWDER ELECTRODES

A. B. Fasman, Academician, Acad. Sci. KazSSR
D. V. Sokol'skii, and K. A. Shurov

S. M. Kirov Abkhaz State University

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Potentiometric studies of the mechanism of catalytic hydrogenation in solutions [1-6] showed that intensely mixed metal powders transfer their potential to a stationary electrode. Similar results were obtained later in [7, 8]. The existence of electron exchange between a stationary electrode and particles bombarding it allowed several authors [9-15] to obtain curves of charging by the impact method. On the basis of these results, Boutry, Bloch, and Balaceanu [16] and Gerischer [17] recently succeeded in the electrical oxidation of hydrogen and electrical reduction of oxygen using small-grained suspensions of catalysts polarized with an auxiliary inert electrode.

In a system with a moving catalyst the stationary electrode is bombarded with continuously renewed charge carriers and there is, in principle, a new possibility of creating a half-cell functioning under load without polarization losses. The experimental half-cell with circulating powder electrodes (Fig. 1) consists of a plexiglass polarization cell 1, a membrane pump 2 operated by an electric motor 3 through a reducing worm gear 4, a generator 5, a system of form removers 6, and a heat exchanger 7. The catalyst suspension is pumped through a nickel screen 8 polarized by a current from an external source; it passes into the regenerator 5 and is saturated with an electromotor active gas. An auxiliary electrode 9 is separated from the working space by a porous glass diaphragm 10. The potential of the screen is measured with respect to the saturated calomel electrode 11.

The polarization characteristics of powder hydrogen electrodes are given in the table.

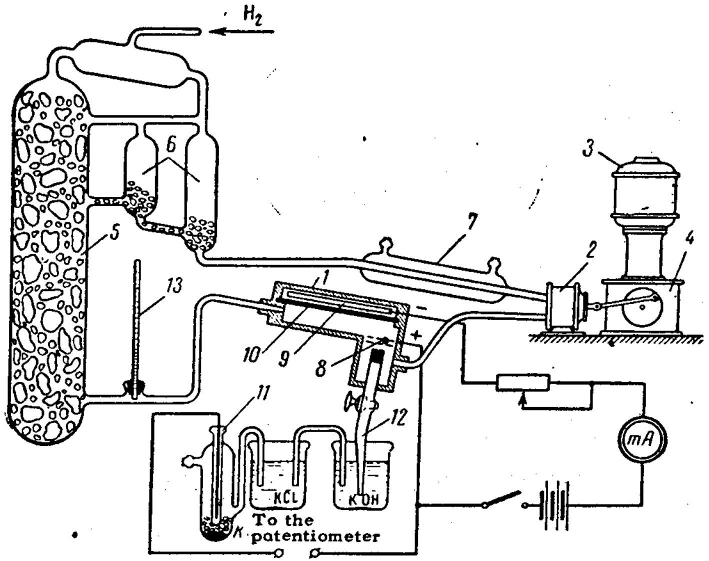

Fig. 1. Diagram of the apparatus for the investigation of the polarization characteristics of powder electrodes.

Polarization Characteristics of Powder Hydrogen Electrodes

| Electrode | Catalyst | Catalyst conc., g/l | Current density, mA/cm$^2$ | Polarization, mV | | | |
|---|---|---|---|---|---|---|---|
| | | | | 20° | 30° | 40° | 50° |
| 30% KOH | Ni | 20 | 20 | 250 | — | — | — |
| | | 40 | 60 | 155 | — | — | — |
| | | 80 | 60 | 70 | 60 | 60 | 60 |
| | | 80 | 120 | 120 | 120 | 115 | 110 |
| | | 80 | 240 | 250 | 240 | 225 | 225 |
| | | 80 | 400 | 350 | — | — | — |
| | | 160 | 60 | 55 | 55 | 55 | 50 |
| | | 160 | 120 | 110 | 110 | 110 | 100 |
| | | 160 | 240 | 230 | 220 | 220 | 205 |
| 5% KOH | Ni | 80 | 60 | 150 | 130 | 110 | 80 |
| | | 80 | 120 | 750 | | 240 | 150 |
| 15% KOH | Ni | 80 | 60 | 130 | 110 | 110 | 90 |
| | | 80 | 120 | 230 | 200 | 190 | 160 |
| 45% KOH | Ni | 80 | 60 | 80 | 80 | 80 | 70 |
| | | 80 | 120 | 155 | 150 | 150 | 150 |
| 40% $K_2CO_3$ | Ni | 80 | 60 | — | — | — | 80 |
| | | 80 | 120 | — | — | — | 210 |
| 30% KOH | Ni (in 30% Ni — Al alloy ) | 80 | 60 | 55 | 60 | 55 | 50 |
| | | 80 | 120 | 120 | 115 | 110 | 100 |
| | | 80 | 240 | 230 | 225 | 200 | 205 |
| 30% KOH | Ni + Zr (2,8%) | 80 | 60 | 50 | — | — | 50 |
| | | 80 | 120 | 95 | — | — | 80 |
| | | 80 | 240 | 180 | — | — | 170 |
| 30% KOH | Pd/Ni (0,8% Pd) | 80 | 60 | — | 60 | 55 | 50 |
| | | 80 | 120 | — | 115 | 115 | 115 |
| | | 80 | 240 | — | 230 | 225 | 215 |

In most of the experiments the catalyst was Raney nickel prepared by boiling a 50% Ni-Al alloy in a water bath for 2 hours.

The data in the table show that the polarization of the electrode decreases considerably when the concentration of the catalyst increases from 20 to 80 g/liter. The optimum concentration of KOH in the electrolyte is 30%. It should be noted that at this concentration the conductivity of the solution is maximum. The volt-ampere characteristics of powder electrodes prepared from 30% Ni-Al and 50% Ni-Al alloys are almost the same. Activation of nickel palladium turned out to be ineffective. The best catalyst for electrical oxidation of hydrogen is Raney nickel containing 2.8% Zr.

The temperature coefficient of polarization is considerably lower than for porous diffusion electrodes [18]; in most experiments it was equal to 0.5-1 mV/deg. The dependence of polarization on temperature increases with decreasing concentrations of KOH in the electrolyte and increasing loads. Successive increases and decreases in the temperature (20–30–40–50–40–30–20°C) in experiments with the same amount of catalyst do not worsen its characteristics; as a rule the polarization of the electrode even decreases 10-20 mV.

During electric oxidation of hydrogen at 20°C the maximum current density is 400 mA/cm$^2$. The powder electrode can be overloaded for a short period of time with a current five times higher (up to 2 A/cm$^2$). As soon as the current is cut off the potential reaches its original value almost instantaneously. Polarization for a long period of time with a very high current (500 mA/cm$^2$ or higher) leads to the expulsion of sorbed hydrogen from the catalyst and to its deactivation.

The powder electrode can function for a long time (the duration of the experiment was 80 hours and more) at $\Delta\varphi$ = 400 mV because the particles of the catalyst retain their original potential because of a short contact with the screen.

During electrical oxidation of CO on the Pd/Ni (0.8% Pd) catalyst i = 60 mA/cm$^2$ at $\Delta\varphi$ = 230 mV (Fig. 2). The CO utilization coefficient is 67.4% –part of the current is spent on the extraction of hydrogen sorbed by nickel. Chemical analysis showed no potassium formate or formaldehyde in the solution. Electrical oxidation of potassium formate in an argon atmosphere (an amount of HCOOK equivalent to 2 liters of CO is introduced into the electrolyte) occurs at higher anode potentials (curve 2). Consequently, CO is oxidized directly to the $CO_3$ anion in alkaline electrolytes at low temperatures [11]. Similar results were described in [19].

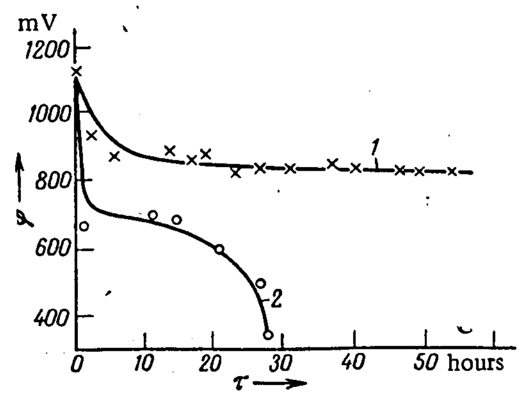

Fig. 2. Functioning of oxide-carbon (1) and formate (2) powder electrodes. The electrolyte was 30% KOH, the temperature 50°C, the catalyst Pd/Ni (0.8% Pd), and the current density 60 mA/cm$^2$.

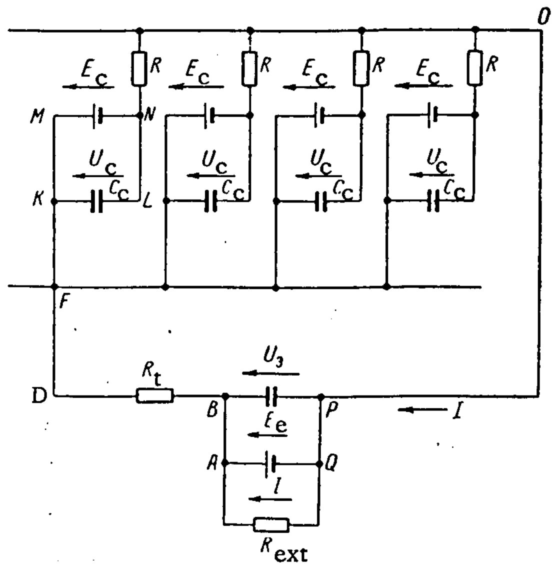

Fig. 3. Equivalent electric diagram of powder electrodes; $E_c$ and $E_e$ are the potentials of the particles of the catalyst and the stationary electrode; $C_c$ and $C_e$ are the capacitances of the double layers of the particles of the catalyst and the electrode; $r_c$ and $r_e$ are the resistances of the double layers of the particles of the catalyst and the electrode; R is the resistance at the point of contact between the particle of the catalyst and the surfaces of the electrode; $R_t$ is the total resistance through which passes the total ionic current of all the n particles of the catalyst in contact at a given moment with the stationary electrode; $U_c$ and $U_e$ are the voltages at the armatures of the capacitors imitating the double layers of the particles of the catalyst and the stationary electrode; $R_e$ is the external resistance.

Using the concept of equivalent electric circuits, one can describe quantitatively the processes occurring in a powder half-cell.

Figure 3 shows an idealized equivalent diagram of an electric circuit created as the result of bombarding a stationary electrode with grains of catalyst suspended in a liquid phase. The particles of the catalyst and the electrode have the capacity of ionizing electromotor active gases, and therefore can create and maintain a difference of potentials in the double electric layer close to the active surface. With some approximation one can assume that the double layer has the property of a plane capacitor, and therefore the electrode-catalyst system can be represented in the equivalent diagram as a series of local emf sources and microcapacitors.

The process of transfer of the potential of the powder electrode to the staionary. electrode at $R_e = \infty$ is described by the equation we obtained earlier [6]. It follows from the apparatus developed in [6] that the power W supplied by the catalyst-electrode system to the load resistance $R_e$ is determined by the following equation (assuming that $E_{cV} = E_e$)*

$$W = \frac{E_e^2}{R_{ext}\left[1 + \frac{r_e(R + nR_t)}{R_{ext}(vnr_e + R + nR_t)}\right]},$$

where v is the linear velocity of the flow.

Investigation of the limits of the function showed that

$$\lim_{v \to \infty} W = \frac{E_e^2}{R_{ext}}.$$

In this case the powder electrode can function as an ideal generator (without any internal losses) in which the coefficient of useful action depends only on the expenditure of power on the circulation of the suspension.

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* The calculations were made in collaboration with A. V. Bykov.

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