

HYDROGEN OXIDATION ON A POROUS NICKEL ELECTRODE*

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The preceding report [1] described the results of research into the oxidation kinetics of hydrogen on a porous nickel electrode and gave a detailed description of the method employed, based on the recording of charging curves.

This paper gives further results of a study of porous nickel electrodes of varying structure.

The electrodes were made from various nickel powders: carbonylic with average particle size of 6 microns, electrolytic with particle size 20 and 60 microns, and ~ 200 micron nickel chips. Ammonium bicarbonate formed the pore-forming filler. A weighed amount of nickel powder was carefully mixed with a defined quantity of the pore-forming agent until a homogeneous mixture was obtained. The layer formed was then subjected to a pressure of 1.5 t/cm^2 . The briquets obtained were fired in a current of hydrogen, normally at 800 to 950° , for one hour. The finished electrodes were disc-shaped (diameter 1.7 - 1.9 cm , thickness of 0.08 - 0.4 cm). The porosity was 39.5 - 76.5% . We also examined cermet bases of non-lamellar factory produced batteries. The characteristics of a smooth nickel electrode were used for comparison. The method of examination was the same as that in [1].

All the tests were conducted at 60° .

Table 1 gives the chief results from our study of nickel electrodes. A comparison of the exchange currents shows that this can vary on different electrodes by a factor of about 20. These differences are due primarily to the firing temperature. Thus for electrodes 1-3 and 14-16, fired at 950° , the exchange current is a minimum. On electrodes 4-12, roasted at 800° , the current is some three times less. The exchange current can be greatly increased if the electrode is oxidized with oxygen, followed by hydrogen reduction at low temperature. For instance, in the case of electrode No. 12, treated in this way, the exchange current was almost quadrupled after a reducing annealing at a temperature of 400° .

On the smooth electrode, the exchange current was $17.0 \cdot 10^6 \text{ A/cm}^2$; the increase is apparently due to annealing of the electrode in a hydrogen current at a low temperature (400°).

The exchange current can also be raised by electrochemical oxidation of the surface followed by cathodic reduction. After the charging curves had been recorded, electrode 7 was oxidized by anodic polarization at 25 mA for 10 min and then cathodically reduced. The exchange current almost doubled. Provided the firing conditions were identical the exchange current remained practically constant for each type of electrode powder, irrespective of the electrode porosity or macroscopic structure. The values for specific capacitance and electrode surface were mutually proportional insofar as a capacitance of $20 \mu\text{F/cm}^2$ was accepted in all cases per 1 cm^2 nickel surface.

The true surface of porous electrodes depends markedly on the degree of dispersion of the initial materials. As the grain size increases, the surface of the electrodes decreases (electrodes 4, 9, 12, 14). There is a slight increase in surface after the electrode is electrochemically oxidized, followed by reduction (electrodes 7 and 8). Maximum surface increase is found after low-temperature reduction of a previously oxidized testpiece (electrodes 12 and 13); this is due to breaking up of the grain surface during treatment.

The Deryagin [2] method was also used to measure the specific surface of some electrodes. Table 2 compares the data obtained by the two independent methods.

These data show that the results agree satisfactorily.

* Second report of a series in this field.

TABLE 1. Characteristics of Nickel Electrodes

Electrode No.	Designation	Firing temp. (°C)	Specific gravity (g/cm ³)	Porosity g (%)	Change in electrical conductivity	Thickness of electrode (cm)	Penetration depth of process x _g (cm)	Derived thickness, δ	Specific capacitance, c · 10 ³ (μF/cm ²)	Specific surface S · 10 ³ (cm ⁻¹)	Exchange current i ₀ (A/cm ²)	Minimum effective resistance R _{eff} · min (SL · cm ²)	Effective resistance for electrode thickness 0.3 cm (Ω · cm ²)
1	A40	950	5.35	40.2	7.7	0.097	0.49	0.20	101.0	5.05	0.91	12.70	23.2
2	A41	950	5.35	40.2	7.7	0.21	0.44	0.49	104.4	5.22	1.18	11.00	19.0
3	A42	950	5.35	40.2	7.7	0.30	0.48	0.62	101.0	5.05	0.91	12.60	23.0
4	A19	800	5.37	39.8	7.4	0.28	0.32	0.88	95.0	4.75	2.28	8.10	11.0
5	A20	800	4.23	52.5	4.43	0.30	0.45	0.66	63.4	3.17	3.00	6.7	
6	A21	800	3.2	64.1	2.95	0.30	0.64	0.46	47.0	2.35	3.15	6.2	
7	A55	800	3.1	65.2	2.9	0.23	0.87	0.34	44.8	2.24	1.68	8.65	25.4
8	A55a *	800	3.1	65.2	2.9	0.23	0.60	0.50	54.0	2.57	3.16	5.88	9.8
9	B28	800	5.4	39.5	0.5	0.295	0.37	0.80	71.4	3.57	2.62	8.20	11.9
10	B29	800	4.15	53.4	4.13	0.31	0.51	0.59	56.0	2.80	2.80	7.20	13.3
11	B30	800	3.12	65.1	2.66	0.30	0.71	0.42	45.6	2.28	2.44	6.80	17.0
12	C57	800	4.35	51.3	4.8	0.30	0.74	0.41	52.4	2.67	2.86	7.80	20.5
13	C57a†	400	4.35	51.3	4.8	0.30	0.18	1.66	96.8	4.84	11.10	2.95	3.2
14	D36	950	4.9	45.0	4.13	0.29	1.88	0.16	20.4	1.02	0.56	26.40	176.0
15	D37	950	3.72	58.2	2.36	0.30	2.63	0.11	17.9	0.89	0.56	21.30	210.0
16	L38	950	2.5	72.1	1.58	0.26	4.67	0.064	13.6	0.67	0.55	20.0	360.0
17	A48‡	700	2.55	71.5	2.32	0.28	0.70	0.42	39.0	1.95	3.90	5.45	13.6
18	A50**	700	2.1	76.5	2.36	0.18	0.82	0.22	57.0	2.85	3.82	4.50	10.2
19	A59††	850	2.24	75.0	2.54	0.20	1.07	0.19	45.2	2.26	2.13	7.05	26.0
20	A61	850	3.35	62.5	3.17	0.30	0.69	0.43	60.8	3.04	1.83	7.40	18.4
21	Smooth	400‡‡	8.9	—	—	—	—	—	0.16	—	17.00	3350.0	3350.0

Note. 'A' indicates electrodes made of carbonylic nickel with 6 μ particles; B and C indicate those made of electrolytic nickel with particles 20 and 60 microns; D refers to nickel chips with particle size 200 microns.

* Electrode A55 was electrochemically oxidized and reduced.

† Electrode C57 was oxidized with oxygen at 400° and reduced with hydrogen at the same temperature.

‡ The electrode was made of carbonylic nickel, with a coarse-grained (160 microns) filler.

** Cermet base of a non-lamellar battery.

†† Cermet base of factory produced alkali batteries.

‡‡ Firing temperature in hydrogen atmosphere.

TABLE 2. Specific Surface of Some Electrode Testpieces

Electrode	Specific surface (cm ² / cm ³)	
	by charging curves	by Deryagin's method
A41	5220	6500
A42	5050	4860
B29	2800	2400
A55a	2570	2500
D36	1020	810
A59	2260	2450

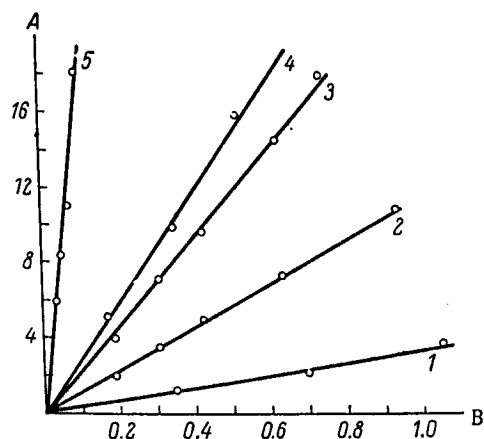
By comparing the size of the surface, determined by the charging curves, with the geometrical surface of the particles as calculated from their mean diameters, the particle surface roughness can be assessed. Table 3 gives these roughness indices.

The roughness coefficients of the powders are related to the method of manufacture. Grains of carbonylic nickel are almost spherical with extreme smoothness. Electrolytic nickel has a dendritic structure while nickel filings are very rough with cracks and torn edges. When an electrode is oxidized and then reduced at low temperature its surface becomes broken; the particle roughness index for electrode 7 rose from 9.1 to 16.5 when treated in this way.

As far as the macroscopic structure of the electrodes studied is concerned, certain conditions are quite pronounced. As the electrode porosity rises, its electroconductivity variation coefficient diminishes. Increase in particle size has the same effect apparently due to the rather loose packing of these types of particles.

TABLE 3. Roughness Coefficients.

Initial nickel powders	Surface roughness coefficient
Carbonylic (particles 6 microns)	1.3
Electrolytic with average particle size 20 microns	4.0
Electrolytic, particles 60 microns	9.1
Electrolytic, particles 60 microns, after oxidation and reduction	16.5
Filings, particles 200 microns	14.2
Smooth electrode with dull surface	7.9



Polarization curves with low polarization for certain electrodes. A) Polarization (mV); B) current density (A/cm²). Electrode: 1) C57a; 2) A20; 3) A42; 4) C57; 5) D36.

x_e varies in a fairly wide range. For the C57a electrode, with a large and very active surface, x_e is about 0.2 cm, whereas in the case of the coarse-grained electrodes, fired at high temperature and therefore low in activity, x_e reaches 2-5 cm.

The relationship between polarization and current density can serve as a direct macrokinetic characteristic of a porous electrode. When the potential shifts slightly from equilibrium the polarization is proportional to the current. The proportion can be regarded as the effective resistance of the electrode:

$$x_e = \sqrt{\frac{b}{2Si_0\eta}}$$

The figure gives a plot of polarization versus current for some electrodes (with correction for concentration polarization); this shows that the slope of the straight lines (effective resistance of the electrode R_{eff}) decreases and activity rises as the degree of dispersion of the powder increases and the firing temperature falls. It is more revealing to compare the effective resistance of electrodes of the same thickness as or considerably thicker than x_e . In the latter case we shall obtain the minimum possible effective resistance for a porous electrode of a particular structure under given conditions $R_{eff \min}$. This formula [3] can serve to calculate the minimum effective electrode resistance:

$$R_{eff \min} = \sqrt{\frac{b_p}{2Si_0\eta}}$$

We will now deal with the macroscopic characteristics of the electrodes. These are determined both by their structural and kinetic properties. Uneven distribution of the charging intensity over a porous electrode can be determined by the δ value — even derived thickness. Where δ is large, the internal surface of the electrode is very unevenly utilized and only a very thin outer layer of the electrode operates [3]. The thickness of this layer is governed by the "effective penetration of the process" — x_e : this shows at what depth within the electrode the intensity of the process is reduced by the factor e . The relation between x_e and the structural and kinetic characteristics of the electrode is as follows [3]:

$$R_{eff} = \frac{\eta_{\infty}}{I}$$

From this formula it may be seen that x_e increases with decreasing resistance of the electrolyte in the pores (p), and decreases as the exchange current specific surface increases.

The x_e values in Table 1 were calculated from experimental charging curves. These data show that for our electrodes

Table 1 gives $R_{\text{eff min}}$ for the electrodes studied; it shows that $R_{\text{eff min}}$ varies fairly widely $3-30 \Omega \cdot \text{cm}^2$. However, it must be borne in mind that $R_{\text{eff min}}$ is only reached with a considerable derived electrode thickness (where $\delta = 2-3$). Here, several electrodes with identical δ have a completely different physical thickness. For example, in the case of C57a $\delta = 2$ with thickness 0.36 cm, while electrode D38 should have a thickness of about 10 cm. The difference between the electrodes is more typical if the effective resistances are compared for electrodes with the same physical thickness, for instance with $l = 0.3$ cm. This conversion can be carried out by means of the graph in [4].

Table 1 gives calculated R_{eff} values with a 0.3 cm thick electrode. These data show that the difference between the electrodes is much more marked in this case (3.2 and 360 ohms $\cdot \text{cm}^2$). For comparison, Table 1 gives these characteristics for a smooth nickel electrode. Its effective resistance (3350 ohms $\cdot \text{cm}^2$) is 1000 times higher than that of the most active of the porous electrodes.

SUMMARY

It is noted that rise in the electrode firing temperature decreases the surface activity (exchange current); oxidation followed by low-temperature reduction breaks up and activates the nickel surface.

It is shown that macroscopic polarization characteristics of porous electrodes are governed both by their kinetic and by their structural properties. This paper compares the electrodes studied with each other and with a smooth nickel electrode. The activity of the best porous electrodes is 1000 times higher than that of the smooth electrode.

LITERATURE CITED

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.
