MEASUREMENT OF THE TORTUOSITY FACTOR OF Ni–Cd BATTERY ELECTRODES BY AN IMPROVED CONDUCTIVITY METHOD

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Summary

The tortuosity factor of pores (f_p) and the porosity (V_p) of nickel–cadmium battery electrodes bonded with polytetrafluoroethylene were determined from the measured true and apparent densities and from the conductivity of the pore electrolyte. The conductivity cell data were evaluated by a new method based on introducing a correction for the screening effect of Luggin capillaries. The influence of the values of f_p and V_p on the transport of ions in the pores and on the electrode performance is discussed.

Introduction

The tortuosity factor of pores, f_p, according to the popular definition, is the ratio of the "actual" length of a pore between two points to their geometric distance. In reality, however, the structure of porous bodies is too complicated to allow a definition of the actual pore length. Therefore, it is better to define f_p by the electrical conductivity, κ_p, of an electrolyte in the pores as follows:

$$\kappa_p = \kappa_e V_p / f_p \tag{1}$$

were κ_e denotes the electrical conductivity of the free electrolyte and V_p the volume fraction of pores in the porous body (porosity), or eventually the volume fraction of drowned pores. An analogous definition is based on diffusion. The value of f_p is larger than one except for the case of an ideal porous body which contains only straight parallel pores (*e.g.*, cylindrical); it can be obtained either by diffusion measurements or, as in the present work, by measurement of the electrolytic conductivity, where use is made of eqn. (1). Our method is based on that of Euler and Rieder [1] and Ksenzhek *et al.* [2].

Principle of the method

A porous membrane (diaphragm) is placed in an electrolyte in a homogeneous electric field, whose lines of force are perpendicular to the diaphragm surface. Two Luggin capillaries are placed at a distance on either side of the diaphragm of uniform, well-defined thickness d_p (Fig. 1). We shall denote
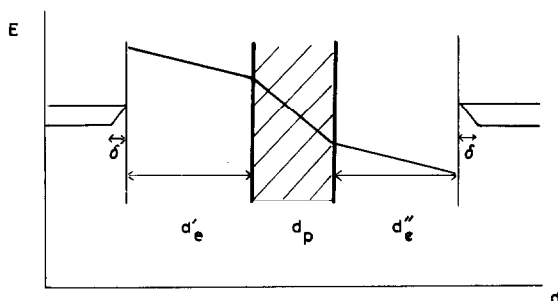

Fig. 1. Scheme of electric field between Luggin capillaries and of measured distances; $d_e = d'_e + d''_e$.

the distance between the tips of the Luggin capillaries as $d_p + d_e$, so that d_e is the length of a line of force in the free electrolyte (equal to $d'_e + d''_e$ in Fig. 1). The potential drop ΔE between the tips of the capillaries observed at a current density i will be given as:

$$\Delta E = i(d_p/\kappa_p + d_e/\kappa_e) \tag{2}$$

where κ_p is the conductivity of the drowned pores and κ_e that of the free electrolyte. If the diaphragm is removed, other conditions being kept the same, the potential drop will change to:

$$\Delta E' = i(d_e + d_p)/\kappa_e \tag{3}$$

whence the value of κ_e can be determined and introduced into eqn. (2) to give κ_p.

In practice, however, the length of the line of force d_e is not precisely defined. Although the distance between the tips of the Luggin capillaries can be determined exactly by means of a suitable gauge, the effective length of a line of force may be slightly different because of irregularities in the shape of the capillary tips and a screening effect. Therefore, d_e in the above equations must be replaced by $d_e + \delta$, where δ is a correction for the shape of the capillary tips. This correction is found by analyzing a series (at least 4) of measurements at varying d_e values and may be positive or negative. Equation (3) can be rearranged to read:

$$\kappa_e = \frac{i}{\Delta E'}\delta + \frac{i}{\Delta E'}(d_e + d_p) = a_k\,\delta + b_k \tag{4}$$

To simplify the notation, we introduce $a_k = i/\Delta E'$, $b_k = (d_e + d_p)i/\Delta E'$, which are coefficients of the linear eqn. (4) corresponding to the kth measurement. Now $d_e + d_p$ is the (mechanically) measured distance between the capillary tips, which is varied to obtain at least four independent measurements, and hence at least four equations of the form (4).

The problem is to find the best possible values of the unknowns, κ_e and δ, to fulfil all the given equations whose number is higher than that of the unknowns. This can be solved by the method of regression analysis; the optimum values of κ_e and δ fulfil the following linear equations:

$$n\kappa_e - \delta \Sigma a_k = \Sigma b_k \tag{5}$$

$$\kappa_e \Sigma a_k - \delta \Sigma a_k^2 = \Sigma a_k b_k \tag{6}$$

where the summation proceeds from 1 to n (i.e., the number of measurements). The solution of this system is numerically very simple, although a general solution would look rather complicated. On introducing the values found for κ_e and δ into the rearranged eqn. (2):

$$1/\kappa_p = \Delta E/d_p i - (d_c + \delta)/d_p \kappa_e \tag{7}$$

we calculate the conductivity of the pore electrolyte κ_p. Finally, the tortuosity factor f_p can be found from eqn. (1) if the porosity of the diaphragm is known. Otherwise the ratio V_p/f_p can serve as a characteristic of the porous structure. We propose for it the term "coefficient of transport hindrance" or "structural factor"; the transport in the diaphragm is slower by this factor than in the free electrolyte.

Experimental

The diaphragm (1) is placed in a cylindrical vessel (Fig. 2) made of poly(methyl methacrylate) glass, consisting of three separate parts held together by cap nuts (2). Disc-shaped auxiliary electrodes (3) are placed on the ends of the cylinder; their diameter is equal to that of the cylinder. Luggin capillaries (4) pass through the cylinder ends and through the auxiliary electrodes; they are joined directly to two equal reference electrodes (without liquid junctions). The ends of the capillaries are diagonally cut to minimize errors in the case where they touch the diaphragm. The sample is sealed with cylindrical silicone rubber gaskets (5) combined with plastic sliding rings to prevent its abrasion. The sample is held in place by a holding nut (6). Cylindrical screens (7) ensure the homogeneity of the electric field between the Luggin capillaries and the diaphragm, and prevent the gases evolved on the electrodes (3) from entering this field. Apertures (8) in the upper part of the cell serve for gas exit. Electric current is led to terminals (9). The three parts of the cell and the Luggin capillaries are sealed with rubber O-rings.
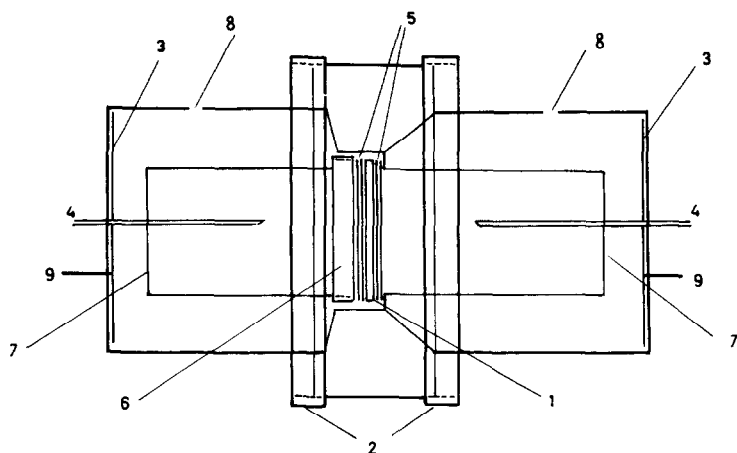
Fig. 2. Scheme of conductivity cell. 1, Measured diaphragm; 2, cap nut; 3, auxiliary electrode; 4, Luggin capillary; 5, silicone rubber gasket; 6, holding nut; 7, screening cylinder; 8, gas outlet; 9, current terminal.

The diaphragm to be measured is first saturated with the chosen electrolyte in a separate vessel connected with a water vacuum pump; it is then transferred to the measuring cell, which is in turn filled with the electrolyte, and left standing for about 30 min to equilibrate the temperature. The potential drop between the Luggin capillaries is then measured at various currents. The $\Delta E-i$ dependence must be linear; if not, polarization of the diaphragm is taking place and this is prevented either by using smaller currents or by changing the electrolyte or deaerating it. Afterwards the sample is removed without changing the position of the Luggin capillaries, and the potential drop $\Delta E'$ is measured and introduced into eqn. (3). Thus, the temperature of the measurement is not important, it should only be kept constant during a run. By measuring the resistance of the cell when a nonporous silicone membrane was inserted in place of the diaphragm, it was proved that leakage currents were negligible. The resistance was of the order of 10^4 Ω whereas with a diaphragm it was lower by three orders of magnitude.

For the studies of Ni–Cd accumulator electrodes, the electrolyte was about 10% KOH. Porosities were determined from the true and apparent densities of the electrodes. The true densities were measured pycnometrically in toluene, the apparent densities in a vacuum mercury densitometer at 900 Torr. The hydrodynamic resistance of the pores was determined by measuring the rate of flow of water using the cell shown in Fig. 2, with a graduated glass tube inserted in one of the apertures (8).

Results and Discussion

The functioning of the apparatus was checked with the aid of an alginate membrane containing parallel, almost cylindrical pores [3], which

gave a value of f_p close to one in accord with expectation ($f_p = 1.03$, $V_p = 0.55$). In addition, a series of compacts pressed and sintered from classified carbonyl nickel powder (3 - 5 μm) gave $f_p = 1.22$ - 1.36 ($V_p = 0.62$ - 0.54), which is close to the theoretical value of $\sqrt{2}$ [4].

The influence of the shape of the capillary tips (the correction δ) is very marked as is evident from the dependence of the conductivity of 10% KOH calculated from eqn. (3) on the distance between the capillaries (Fig. 3). With increasing distance the calculated value of κ_e approaches the tabulated one. (It is, however, not recommended to measure with capillaries too far away from the sample since the difference between the measurements with and without the diaphragm would then be relatively small and the results would be subjected to large experimental errors.) After calculating the correction $\delta = 0.115$ cm from eqns. (5) and (6), corrected values of κ_e were obtained from eqn. (4), which are plotted in the upper part of Fig. 3. Thus, the importance of the correction δ is clearly demonstrated.
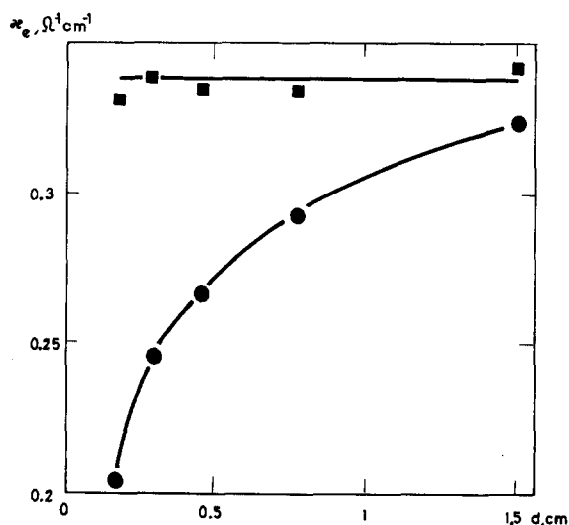

Fig. 3. Dependence of measured electrolyte conductivity on distance between Luggin capillaries. ● κ_e calculated from eqn. (3); ■ from eqn. (4).

Typical results obtained with cadmium electrodes bonded with 10% polytetrafluoroethylene (PTFE) [5] are given in Table 1. The electrodes contained a current collector, which was an iron grid ("expanded-metal") with a relative area of the openings of 0.52 (calculated from the weight per cm^2, thickness of the iron sheet 0.025 cm, and its density 7.85 g/cm^3). To estimate the influence of the current collector on the measured tortuosity factor, measurements were made in the conductivity cell with the expanded-metal grid alone. No difference in the resistance with and without the iron grid was detected, so it was concluded that the current collector did not influence the tortuosity factor of the electrodes; in other words, its effect on the transport of ions was negligible. A certain effect of the iron

TABLE 1

Values of electrode thickness d_p (cm), conductivities of electrolyte in the bulk, κ_e, and in the pores, κ_p (Ω^{-1} cm^{-1}), apparent and true densities, ρ_a and ρ_t (g/cm^3), porosity, V_p, and tortuosity factor, f_p.

No.	d_p	κ_e	κ_p	ρ_a	ρ_t	V_p	f_p
Cadmium electrodes							
1[d]	0.209	0.324	0.0543	1.85	4.46	0.585	3.47
				1.89	4.47	0.577	
2[ch]	0.195	0.333	0.120	1.80	5.60	0.679	1.88
				1.80	5.50	0.673	
3[d]	0.214	0.345	0.0606	1.85	4.63	0.600	3.42
				1.84	4.60	0.600	
4[ch]	0.106	0.346	0.0920	1.82	5.51	0.670	2.52
				1.85	5.59	0.669	
Nickel oxide electrodes							
5[d]	0.296	0.321	0.0099	1.43	2.86	0.500	16.1
				1.41	2.80	0.496	
6[ch]	0.340	0.339	0.0232	1.22	2.76	0.558	8.2
				1.20	2.76	0.565	
7[d]	0.319	0.317	0.0145	1.40	2.85	0.509	11.1
				1.43	2.87	0.502	
8[ch]	0.336	0.385	0.0210	1.30	2.84	0.542	9.6
				1.37	2.79	0.509	
9[a]	0.260	0.348	0.0113	1.55	2.93	0.471	14.5
				1.55	2.94	0.473	
10[a,b]	0.260	0.363	0.0259	1.55	2.94	0.473	6.6
11[d]	0.200	0.382	0.0296	—	—	(0.42)[c]	5.4
12[d]	0.205	0.347	0.0276	—	—	(0.42)[c]	5.3
13[ch]	0.242	0.347	0.0650	—	—	(0.5)[c]	2.7
14[d,e]	0.202	0.352	0.0357	1.61	2.78	0.421	4.2
15[d,e]	0.205	0.360	0.0332	1.61	2.79	0.423	4.6

[a]Non-cycled electrode; [b]the electrolyte contained 5 drops of a saponate detergent per 2000 ml; [c]assumed values; [ch]charged electrode; [d]discharged electrode; [e]0.012% Triton X-100 in 10% KOH.

grid on the pore electrolyte conductivity can be nevertheless expected if the electrode thickness is about the same as that of the current collector. This is probably the case in the fourth line of Table 1, where the f_p value is appreciably higher than in the second line. In practice, however, the cadmium electrodes are loaded with current from both sides, whereby the screening influence of the current collector is eliminated.

The tortuosity factor of discharged electrodes is considerably higher than that of the charged ones, although the difference found in porosity is small. This suggests that the cadmium hydroxide is present in the discharged electrodes in a hydrated, somewhat swollen form, which shrinks on drying before the porosity measurements. Hence, the porosity of discharged elec-

trodes in the hydrated state is probably lower than indicated in Table 1 (Nos. 1 and 3).

To determine the content of hydrophobic pores, the true density of the active material (from non-cycled electrodes) was measured also in a water pycnometer and compared with the value measured in toluene. It turned out that about 10% of the pores were not wetted with water, hence the "liquid porosity" was equal to $V_p - 0.1$.

Nickel oxide electrodes bonded with a mixture of PTFE and acetylene carbon black [6] are typically semihydrophobic. When the measurements were performed on discs cut out from washed and dried rectangular electrodes, the electrolyte conductivity in the pores reached a stationary value only after the sample to be measured had stood for a day in the conductivity cell; passage of electric current through the pores apparently favoured this equilibration. Nevertheless, the tortuosity factor attained unusually high values (Table 1, Nos. 5 - 9). The content of hydrophobic pores in non-cycled electrodes was determined, by the same method as with the cadmium electrodes, to be approximately 14%, and that of the hydrophilic ones 33%, i.e., $V_p = 0.33 + 0.14 = 0.47$. After adding a detergent to the electrolyte, at a low concentration so as to prevent excessive foaming, the conductivity reached a stationary value much more rapidly as was evidenced by the values of f_p decreasing gradually from 9.6 to 6.6 (Table 1, No. 10). The latter value suggests that the porous structure is far from the ideal one; there are probably larger pores surrounded by smaller ones causing a transport hindrance, similar to the case of electrodes made from active carbon. Both this circumstance and the imperfect drowning of the pores are responsible for the high f_p values obtained with electrodes Nos. 5 - 9.

When, on the other hand, the measurements were performed on disc-shaped electrodes which were placed in the measuring cell immediately after four charge–discharge cycles, the ionic conductivity in the pores quickly reached a stationary value and the tortuosity factor was much smaller (Table 1, Nos. 11 - 13) suggesting that the pores were more filled with the electrolyte. Finally, when the electrolyte used during cycling and measuring the conductivity contained a detergent, the tortuosity factor dropped still more, although not substantially (Table 1, Nos. 14 and 15). A similar result was obtained after filling the electrode pores by boiling for 1 h in water and then equilibrating with 10% KOH for 3 days, giving $f_p = 4.4$, which can hence be considered as the limiting value at full drowning of the pores.

Since the cycled nickel oxide electrodes contain various more or less hydrated hydroxides of nickel, which are known to have a gel-like consistency and shrink on drying, porosity measurement is a difficult task. The higher V_p values (Nos. 5 - 8 in Table 1) correspond to electrodes dried at 105 °C, the lower ones (Nos. 14 and 15) to those dried at room temperature in vacuum, where the shrinking of the gel was less pronounced, although it did occur as was evidenced by the fact that the electrode thickness decreased by several percent.

The tortuosity factor of the charged electrodes is significantly less than that of the discharged electrodes. The molar volume of NiOOH (19.0 cm^3/mol) is less than that of Ni(OH)$_2$ (22.6 cm^3/mol) [7] but the difference is rather small reflecting the small differences in the values of V_p. However, if the porosity of the electrode in the hydrated state is much less than in the dry state, then even small differences in the molar volume of the gel may be significant for the ionic conductivity of the pores (we assume that the ionic conductivity of the hydroxide gel is much smaller than that of the electrolyte).

The measurements of the ionic conductivity were supported by measurements of the hydrodynamic resistance. If we denote the rate of flow of water (containing 2 drops of a saponate detergent in 250 ml) through the pores of a charged electrode as 100, then with a discharged one it was equal to 48 at the same pressure gradient, and in accord with the drop in the ionic conductivity. When, however, the discharged electrode was dried at 105 - 120 °C, the rate of flow of water through the pores increased to 151, evidence of the shrinking of the nickel hydroxide gel; and after three hours it dropped again to 108 as the gel apparently swelled somewhat in water.

Conclusions

The proposed improved method of conductivity measurements enables the coefficient of transport hindrance in the pores (ratio of the conductivity of the pore electrolyte to that of the free electrolyte) to be evaluated, which is related to the electrode performance at higher current densities. The tortuosity factor of the pores can be obtained as the ratio of the porosity to the coefficient of transport hindrance. Application of the new method to porous electrodes helps to obtain a better insight into their porous structure and transport properties.

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