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Partially immersed gas-diffusion electrodes

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A new type of partially immersed carbon gas-diffusion electrode with a sandwich-like structure consisting of two active layers each side of the gas-supplying layer is described. The current collector grid is embedded into the electrically conductive gas-supplying layer. A theoretical model of the partially immersed electrodes is proposed and experimentally confirmed. The model can be used for the theoretical prediction of the steady state behaviour of partially immersed electrodes from experimental data obtained with non-immersed gas-diffusion electrodes. An experimental zinc–air battery of 1900 A h capacity with the new type of partially immersed carbon air gas-diffusion electrodes has shown a specific energy density of 250 W h kg^{-1} and 420 W h l^{-1} at a current density of 0·5 mA cm^{-2}.

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1. Introduction

Wetproofed gas-diffusion electrodes are used in different types of electrochemical power sources: fuel cells, metal–air systems, etc. These electrodes are porous membranes which usually also constitute the wall of the cell. In this normal type of operation the gas-diffusion electrode separates the reacting gas from the electrolyte and the whole projected area of the electrode is in contact with the gas. This is essential for high current density operation of the gas-diffusion electrode. However, being part of the cell case the electrode should meet several requirements including sufficient mechanical strength to withstand the electrolyte hydrostatic pressure. Any local damage to the electrode will cause the electrolyte to drain off from the cell and this could be critical for the practical application of the cell.

The above disadvantage is eliminated if the gas-diffusion electrode is designed as a partially immersed electrode and not as the wall of the cell. For this type of operation the gas-diffusion electrode is immersed into the electrolyte in such a way that only a small part of it remains above the electrolyte level and is in contact with the working gas. The reactant gas enters the electrode through this relatively small contact surface and is transported to the immersed part of the electrode through pores free of electrolyte.

Partially immersed gas-diffusion electrodes are used in some zinc–air batteries [1, 2] and some hydrogen–oxygen fuel cells [3]. These electrodes are prepared from active carbon (in some cases mixed with catalysts) and are wetproofed with hydrophobic agents.

The discharge rate of immersed porous gas-diffusion electrodes is restricted mainly by the rate of gas transport and with air it is about 1 mA cm^{-2}. For electrodes operating with pure oxygen or pure hydrogen this value is much higher. The lifetime of these carbon gas-diffusion electrodes is usually limited by a process of flooding of their pores with electrolyte.

The present paper is concerned with an investigation of a new type of wetproofed carbon gas-diffusion electrodes designed for partially immersed operation.

The electrode developed in this laboratory [4] has a sandwich-like structure consisting of two porous active layers covering both sides of a porous hydrophobic gas-supplying layer. The gas-supplying layer is made of a special electrically conductive hydrophobic material (carbon black wetproofed with PTFE) [5]. The active layers consist of a mixture of the same hydrophobic material plus active carbon catalyst. The current collector grid is embedded into the gas-supplying layer.

This type of gas-supplying layer made from porous hydrophobic material has several advan-

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tages. It has excellent water-repellent properties which completely prevent the penetration of the electrolyte and ensures an extremely long operating life of the immersed electrode. In addition, the well-known effect of 'nitrogen blanketing' is absent because molecular (Knudsen) diffusion is the main type of gas-transport through this porous hydrophobic material at atmospheric pressure [6].

2. Theoretical

The idealized model for the partially immersed gas-diffusion electrode is shown in Fig. 1. The model electrode consists of a gas-supplying layer thickness d, and an active layer, thickness x_0. The whole electrode is immersed into the electrolyte apart from its upper surface which is in contact with the bulk gas. The depth of immersion of the electrode is l. The reactant gas enters the electrode through the upper surface of the gas-supplying layer (with surface area $S = ad$).

During operation the gas is transported in the gas phase along the gas-supplying layer (along the co-ordinate y) and towards the active layer (along the co-ordinate x), dissolves into the electrolyte soaked into the active layer and diffuses to the active sites of the catalyst where the electrochemical reaction is taking place: the generated ionic current flows through the electrolyte soaked into the active layer.

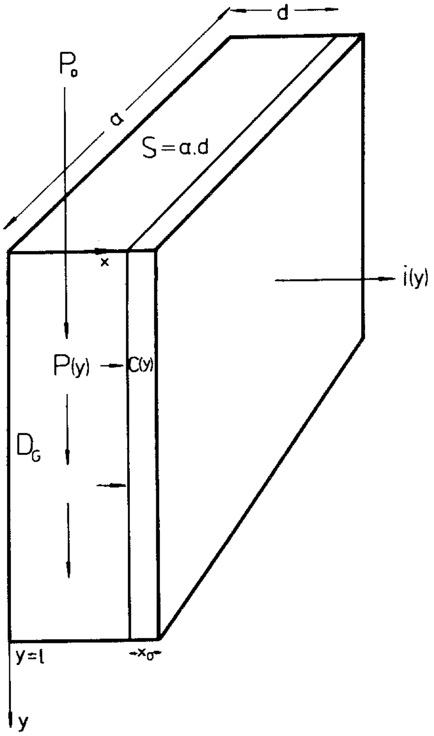

Fig. 1. Idealized model for a partially immersed electrode.

For the mathematical treatment it is assumed that:

(a) The reactant gas is transported along the gas-supplying layer by molecular (Knudsen) diffusion with an effective diffusion coefficient D_G and its partial gas pressure $P(y)$ is a function of the co-ordinate y only (the gas transport towards the active layer is a fast process).

(b) The reactant gas dissolution and the transport of the dissolved reactant species to the active sites are fast processes so that the concentration $C(y)$ of the dissolved reactant is constant along the thickness of the active layer (along the co-ordinate x) and depends only on the local partial pressure of the reactant gas $[C(y) = kP(y)]$.

(c) The concentration of the electrolyte is constant throughout the whole thickness of the active layer.

(d) There is no IR-drop in the electrode so that the catalyst surface is an equipotential one.

(e) The IR-drop in the electrolyte soaked into the active layer is negligible so that the polarization η is constant throughout the whole electrode–electrolyte interface.

(f) The current $i(y)$ generated from unit surface area of the catalyst is proportional to the local reactant concentration $C(y)$ and for sufficiently high overvoltage is given by

$$i(y) = i_0 \frac{C(y)}{C_0} \exp\left(\frac{\alpha zF}{RT}\eta\right) \qquad (1)$$

where i_0 is the exchange current density per unit catalyst surface area, α the transfer coefficient, F the Faraday, R the gas constant, T the absolute temperature and $C_0 = kP_0$ the solubility of the reactant at a partial bulk gas pressure P_0.

Under these assumptions the steady-state diffusion through the gas-supplying layer with simultaneous consumption (electrochemical reaction in the active layer) is described by the equation

$$SD_G \frac{d^2P(y)}{dy^2} - \frac{\gamma i_0 x_0 a}{nF} \frac{P(y)}{P_0} \exp\left(\frac{\alpha zF}{RT}\eta\right) = 0 \qquad (2)$$

where γ is the catalyst surface area in contact with the electrolyte per unit volume of the active layer and n the number of electrons involved in the electrochemical reaction.

The boundary conditions for Equation 2 are

$$P = P_0 \quad \text{at} \quad y = 0 \qquad (3)$$

$$\frac{dP}{dy} = 0 \quad \text{at} \quad y = l \qquad (4)$$

and express the fact that the reactant gas pressure at the upper surface of the gas-supplying layer is equal to that in the bulk gas (Equation 3) and the assumption that the gas flow is equal to zero at the lower surface of the gas-supplying layer (Equation 4) (there is no bubbling or dissolution of the reactant gas into the bulk electrolyte).

The solution of Equation 2 under the boundary conditions in Equations 3 and 4 is

$$P(y) = P_0 \frac{\cosh[\beta(l-y)]}{\cosh(\beta l)} \qquad (5)$$

where

$$\beta = \left[\frac{\gamma i_0 x_0 a}{\mathrm{S} nFD_G P_0} \exp\left(\frac{\alpha zF}{RT}\eta\right)\right]^{1/2}. \qquad (6)$$

The total current I generated from the electrode can be calculated from the relation

$$I = nFSD_G \left(\frac{dP}{dy}\right)_{y=0} \qquad (7)$$

From Equations 5 and 7 the total current, I, is given by

$$I = nFD_G P_0 S\beta \tanh(\beta l) \qquad (8)$$

The reciprocal value of β (Equation 6)

$$L = \beta^{-1} = \left[\frac{\gamma i_0 x_0}{dnFD_G P_0} \exp\left(\frac{\alpha zF}{RT}\eta\right)\right]^{-1/2} \qquad (9)$$

has a dimension of length and can be regarded as a specific length L which characterizes the gas transport process in a partially immersed electrode.

If the characteristic length

$$l_D = (nFD_G P_0/\gamma i_0)^{1/2} \qquad (10)$$

of the process of gas transport in the porous hydrophobic structure of the gas-supplying layer, previously defined by one of the authors [7] is substituted into Equation 9, the expression for L acquires the form

$$L = l_D (d/x_0)^{1/2} \exp\left(-\frac{\alpha zF}{2RT}\eta\right). \qquad (11)$$

The specific length L depends on the characteristic length l_D, on the dimensions d and x_0 of the electrode on the polarization η and on the value of $\alpha zF/(2RT)$.

When the specific length L (Equation 9) is used, the expression for the total current generated from the electrode (Equation 8) can be rewritten in the form

$$I = \frac{nFD_G P_0 S}{L} \tanh(l/L). \qquad (12)$$

At sufficiently large values of the argument ($l/L \gg 1$) the total current will tend to the saturation current

$$I_\infty = \frac{nFD_G P_0 S}{L} \qquad (13)$$

The saturation current I_∞ depends on the polarization η through L.

3. Experimental

Partially immersed gas-diffusion electrodes with the structure described above were investigated when operating with oxygen from the air. The gas-supplying layer was made from carbon black wet-proofed with 35% PTFE and was 3 mm thick. The active layer was prepared from a mixture (21 mg cm^{-2}) of the above hydrophobic material plus active carbon NORIT NK promoted [8] with silver (0·7 mg cm^{-2} Ag) taken in a weight ratio of 1 : 2. The electrodes were 8 cm wide and 14 cm high and were produced by hot pressing. Nickel-plated iron grid was used as the current collector.

The current–voltage characteristics of the electrodes in 7 M KOH at room temperature were measured in a half-cell arrangement. The counter electrode was a nickel grid. A Hg/HgO reference electrode was used throughout.

The gas-diffusion electrode was immersed into the electrolyte in such a way that only about 1 cm of it projected above the electrolyte level and was in contact with air. Before the beginning of the experiment the electrode was polarized at a constant cathodic current (about 1 mA cm^{-2}) for a period sufficient to reach a steady state. Following this pretreatment, steady state current–voltage characteristics were measured at a given immersion depth. After the measurement at a particular depth of immersion, the electrode was taken out of the electrolyte, its height was diminished by cutting

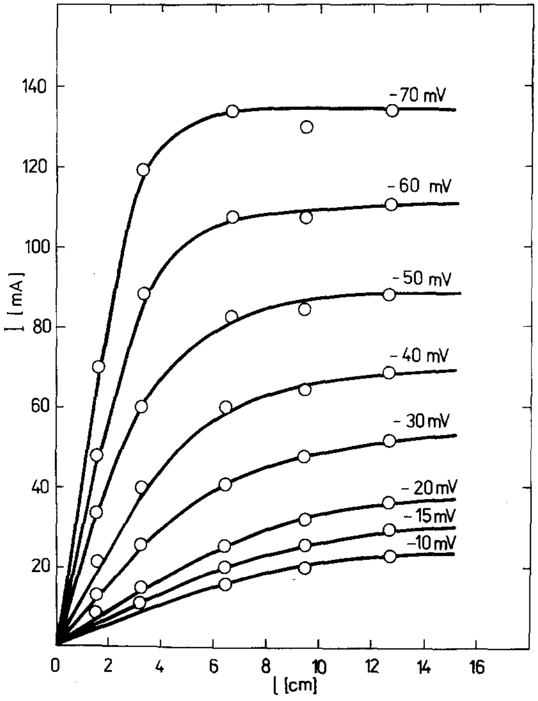

Fig. 2. Experimental curves of the current from a partially immersed gas-diffusion electrode versus depth of immersion at several potentials.

off the lower part and it was re-immersed in such a way that the same part of the electrode was in contact with air. In this way a series of current–voltage characteristics corresponding to several depths of immersion were obtained. From this series of curves the current generated at each potential was obtained for different depth of immersion.

Fig. 2 presents typical experimental curves of the current as a function of the immersion depth for several potentials. At small depths of immersion the curves show a linear increase of the current with the increase of the depth, but the current tends to a limiting value at larger depths of immersion. With the increase of the polarization this saturation current increases and it is reached at a smaller immersion depth.

By using the experimental value of the saturation current I_∞ the specific length L can be calculated from

$$L = nFD_GP_0S/I_\infty \,. \tag{14}$$

The value of the product nFD_GP_0 in Equation 14 can be experimentally determined from the limiting current density

$$I_\delta = nFD_GP_0/\delta \tag{15}$$

at a non-immersed gas-diffusion electrode operating normally with a thick gas-supplying layer (thickness δ) so that the gas transport through this layer is the limiting process. In our case the experimental value was $nFD_GP_0 = 165\,\mathrm{mA\,cm^{-2}}$.

The value of L calculated from Equation 14 with the experimental data (Fig. 2) are plotted as a function of the potential in Fig. 3 (curve 1). As expected from Equation 11 they lie on a straight line on a semi-logarithmic scale.

According to the theoretical model (Equations 12 and 13), the ratio

$$I/I_\infty = \tanh{(l/L)} \tag{16}$$

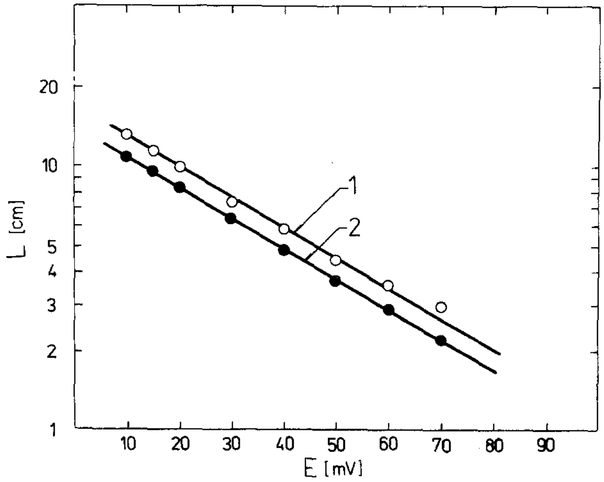

Fig. 3. Specific length L as a function of the potential E. Curve 1 calculated from Equation 14 with the experimental data for partially immersed gas-diffusion electrode (from Fig. 2); curve 2 calculated from Equation 9 with experimental data for a non-immersed gas-diffusion electrode.

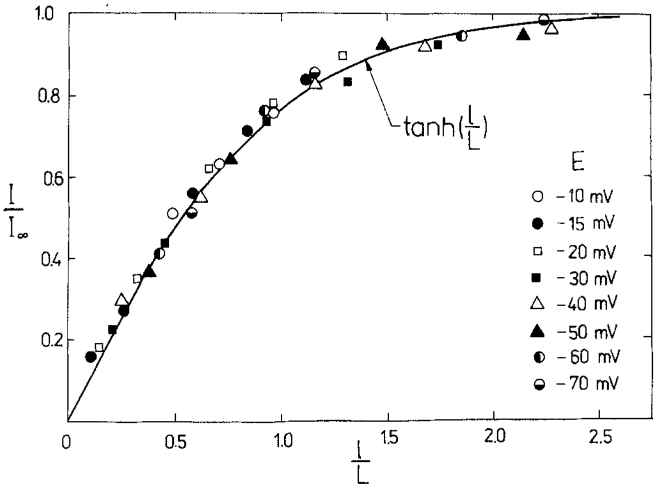

Fig. 4. Comparison of the theoretical curve tanh (l/L) (Equation 16) with the experimental data for I/I_∞ from Fig. 2. The specific length L is calculated from Equation 14 (Fig. 3, curve 1).

will depend only on the reduced (dimensionless) depth of immersion l/L.

The theoretical curve (from Equation 15) and the experimental points from Fig. 2 are presented on Fig. 4 in dimensionless co-ordinated I/I_∞ and l/L. The good agreement of the experiment with the theory is apparent, from which it can be concluded that the proposed simplified model describes adequately the behaviour of the partially immersed gas-diffusion electrodes developed in this laboratory.

The specific length L can also be calculated from Equation 9 with data from independent experiments with non-immersed gas-diffusion electrodes. The value of nFD_GP_0 and $\gamma i_0 x_0$ exp $[\alpha zF/(RT)\eta]$ can be determined from the limiting current density I_δ (Equation 15) of an electrode with a thick gas-supplying layer and from the Tafel plot (obtained at low current density) of an electrode with the same active layer as the immersed electrode. The specific length L calculated from such experiments as a function of the potential is also shown on Fig. 3 (curve 2). The points lie on a straight line parallel to that obtained with the immersed electrode (curve 1) but with a small shift towards the lower values of L. Nevertheless, the application of Equations 9 and 12, respectively, for determining L and for theoretical prediction of the behaviour of partially immersed electrodes is very useful for practical purposes because experiments with non-immersed electrodes are much simpler and quicker than experiments with immersed electrodes.

From Fig. 3 it is obvious that at low polarizations the value of the specific length L is about 10 cm, so that a reasonable depth of immersion l can be of the same order of magnitude, which is important for the practical utilization of the electrodes.

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