

DISTRIBUTION AND MOVEMENT OF ALKALINE ELECTROLYTE IN OXYGEN ELECTRODES

J. JINDRA, J. MRHA and M. MUSILOVÁ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, Prague 10*

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The quantity and distribution of electrolyte in the active layer of a carbon partly water-repellent cathode are, in the range up to 50 mA/cm², independent of the magnitude of current load. As the current load increases, a concentration gradient forms in the electrolyte inside the electrodes whereby osmotic pressure occurs tending to the gas side of the electrode. The osmotic pressure may induce penetration of electrolyte even through a strongly hydrophobic gas layer.

Preparation of thin light-weight membrane electrodes capable of long term operation as cathodes for the reduction of air oxygen, and working without overpressure or forced streaming at relatively high current loads, belongs to one of the fields of electrochemistry where remarkable progress has been achieved during the recent years. The original, at present already classical design of electrodes, characterized by the advancement of the three-phase boundary where the lifetime of the electrodes was a function of the electrode thickness has lost ground to an electrode with a practically stable position of this boundary. The essence of the latter is a combination of a hydrophobic porous gas layer with a hydrophilic porous active layer¹. Virtually all oxygen electrodes prepared today for higher current loads are a version of the above idea.

In practice, there are several problems inherent in the utilization of these electrodes, especially: 1) formation of gas bubbles in the active layer facing the electrolyte (bubbling effect)²⁻⁵; 2) penetration of drops of electrolyte through the gas layer of the electrode (weeping effect)^{6,7}. Either of these problems is subject to the aforementioned combination of the two porous layers of markedly different wetting properties. The former problem has recently received much attention whereas no attention has been paid to the latter. The present paper, therefore, aims to elucidate the reasons inducing the penetration of electrolyte through the otherwise strongly hydrophobic electrode gas layer.

EXPERIMENTAL

The mode of preparing the electrodes was described in previous papers^{8,9}. In all cases, pure active carbon without doping was employed. Teflon was used both as binding agent and to prepare the gas layer. Gas layers A and B had strongly different porous structures. Disc electrodes of 31 mm diameter and a maximum thickness of 1 mm were provided with a nickel gauze on the electrolyte side, serving as a current collector. Measurements were made in 1 and 6M-KOH

against a Hg/HgO reference electrode in the same electrolyte. The Luggin capillary was touching the active layer of the electrode. The electrodes were operating as so called air-breathing electrodes, *i.e.* on air oxygen without forced streaming or overpressure and without cleaning the gas. In other measurements, oxygen of 1–2 cm H₂O overpressure was fed alongside the electrode gas layer. In a half-cell arrangement, nickel plates were used as counterelectrodes. The amount of electrolyte in the test vessel was approximately 25 ml. The quantity of electrolyte which penetrated through the active layer was determined by measuring its volume in a calibrated flask and by subsequent titration with HCl. The electrolyte imbibed into the active layer was determined by weighing. To determine the range and mode of distribution of the electrolyte in the active layer, the porous structure of the layers was measured by mercury penetration¹⁰ at -20°C before and after contact with the alkaline electrolyte. The low temperature enables one to apply the mercury penetration method to samples wetted with electrolyte, due to the fact that the 1M-KOH solution is at this temperature solidified. The freezing has to be done quickly to prevent separating water from the electrolyte by crystallization. For this reason, liquid nitrogen was used as cooling agent. Samples of the active layer were placed into the dilatometer, quickly evacuated and then cooled for 1 hour to -196°C . The dilatometer was filled with mercury at the temperature of the porosimetric measurement proper, *i.e.* at -20°C . Precautions were taken to maintain the temperature at a constant value to eliminate the potential thermometer effect of the dilatometer which might otherwise occur due to the relatively large volume of mercury and the narrow capillary of the dilatometer.

RESULTS AND DISCUSSION

Electrodes prepared at constant conditions were first galvanostatically loaded with 30 mA/cm^2 (related to the geometric surface area of the electrodes inclusive the parts covered with the gasket and current collector) in KOH for 2 h. Polarization curves were then measured on both air and oxygen electrodes. Polarization curves then served as a basis for calculating the curves expressing the dependence of the changes in the electrode potential (ΔE) on the current density, brought

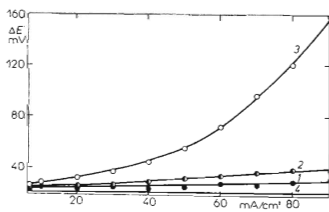


FIG. 1

Potential Difference ΔE due to Switching from Air to Oxygen vs Current Density (after 2 h of operation at 30 mA/cm^2)

Active layer 1 without gas layer; 2 with layer A; 3 with layer B; 4 theoretic value according to Berl.

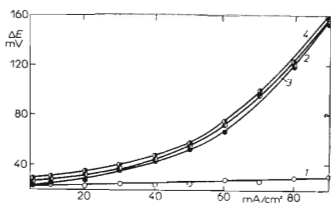
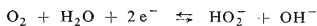


FIG. 2

ΔE vs Current Load after 2 and 50 Hours of Operation at 30 mA/cm^2

1 Active layer without gas layer after 2 h function; 2 after 50 h function; 3 active layer with gas layer B after 2 h function; 4 after 50 h function.

about by switching air to pure oxygen. Neglecting the influence of concentration polarization and assuming the validity of Berl's reaction¹¹



a value of $\Delta E = 21\text{mV}$ ¹² may be expected.

Curves plotted in Fig. 1 suggest that electrodes without gas layers (curve 1) are close to theory. The contribution of concentration polarization to the overall polarization of this electrode is surprisingly small. The influence of concentration polarization in electrodes with a gas layer is, on the other hand, pronounced. Especially the variations in the mode of preparation of this layer are conspicuous (curves 2, 3). Different results were obtained on electrodes without gas layers after 50 hours of operation at 30 mA/cm² (Fig. 2). After 30 minutes already a large amount of minute electrolyte drops could be observed. The size of the drops increased considerably as the current load increased, and after c. 10 hours of operation the drops were flowing down the outer gas layer. Eventually, a thin film of electrolyte covered the total gas side of the electrode. After 50 hours of operation, the presence of the film made itself apparent by a strong increase in the concentration polarization (Fig. 2, curves 1, 2). In electrodes provided with a gas layer, the dependence of concentration polarization on time was negligible (Fig. 2, curves 3, 4). It is of interest, however, that even those electrodes which were covered with a film of electrolyte were capable of reducing oxygen. This enabled us to measure quantitatively the volume of electrolyte which penetrated through the active layer as a function of the current load.

Preliminary determinations suggested a dependence of the volume of electrolyte penetrated through the active layer, on the galvanostatic load in an air electrode^{12,13}. In the present investigations, electrodes without gas layers operating on air were loaded with 0, 10, 30, and 50 mA/cm² for 40 hours in 1M-KOH. The quantity of the electrolyte flowing down the gas side of the electrode within 16–40 h was measured. A large amount of measurements yielded the following mean values of the quantities of electrolyte:

i , mA/cm ²	0	10	30	50
m , mval KOH/24 h	0	4.4	7.5	14.0

Unloaded electrodes had the gas layer covered with a uniform network of tiny electrolyte drops whose volume, however, exhibited no further increase after 40 h. On the contrary, carbonization and crystallization of KOH due to evaporation of water made itself apparent on the surface of the droplets.

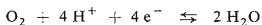
The results obtained may be explained in the following way: As a consequence of the contact between the gas side of the electrode with the ambient air and especially when loaded (due to the reduction of oxygen in an alkaline medium) a concentration gradient is formed in the pores of the active layer filled with electrolyte, whose magnitude increases with the increase of the current load. The concentration gradient induces a difference of chemical potentials of water in the proximity of the three-

phase boundary (μ_1) and in the bulk electrolyte (μ_2). The formation of an osmotic pressure^{14,15} tending from the electrolyte to the gas side of the electrode is the condition of establishment of an equilibrium of both the potentials (x – mole fraction of water):

$$\mu_1 = \mu_0 + RT \ln x_1, \quad \mu_2 = \mu_0 + RT \ln x_2$$

for $x < 1$ is $x_2 < x_1$.

This consideration is supported by the first tests we made on oxygen electrodes working in 4.5N-H₂SO₄. On these electrodes, even when without gas layers, no drop formation was observed after 500 hours of operation¹⁶. In this case, the direction of the osmotic pressure with respect to the overall reaction



is just the contrary.

In electrodes with gas layers, the advancement of the alkaline electrolyte is to a great extent limited or even made impossible. In this case, a strong hydrostatic

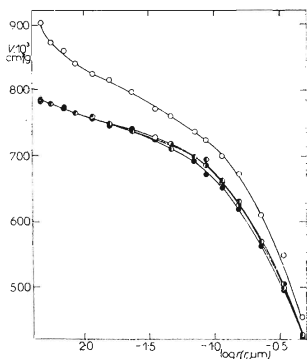


FIG. 3

Integral Porosimetric Curves of Active Layers

○ Active layer without contact with electrolyte ("dry electrode"); current density (mA/cm²): 0 (●); 10 (◐); 30 (◑); 50 (◒).

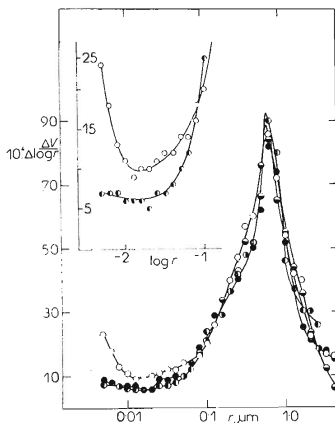


FIG. 4

Differential Porosimetric Curves of Active Layers with an Enlarged Section for $r < 0.1 \mu\text{m}$

For description of curves see Fig. 3.

pressure was observed at the boundary between the active and gas layers, which sometimes led to separation of the two layers. The gap resulting in this way was filled with electrolyte of a considerable overpressure. If the adhesion of both layers is good, the drops of electrolyte are in some cases forced through the gas layer. An increase in the current load of the electrode, therefore, brings about increased requirements on the mutual adhesion of both layers as well as on the porous structure of the gas layer which has, at the same time, to take care of free access of oxygen and departure of inert nitrogen.

The distribution of electrolyte and its total quantity in the active layer was further studied in dependence on the current load. The results obtained were compared to those obtained by penetration of mercury on dry active layers. The results were compiled in Table I and in Fig. 3, and 4. Fig. 3 depicts the integral, Fig. 4 the differential porosimetric curves of samples of active layers operating as air cathodes at 0, 10, 30, and 50 mA/cm². Fig. 3 gives the region of transition pores and a part of the micropores interesting for judging the distribution of the electrolyte in the porous skeleton of the active layer. Fig. 3 and 4 show unanimously that the fall in the overall porosity may be ascribed solely to the decrease in the pores of $r < 0.5 \mu\text{m}$; these pores are filled with electrolyte. The distribution of larger pores is, within experimental error, equal in all samples (Fig. 4, Table I). In all cases, these pores are formed by intergranular voids between active carbon and teflon. Porosimetric measurements further imply that both the quantity of imbibed electrolyte and its distribution in the

TABLE I

Volumes of Mercury Pressed into Active Layers Wetted and Unwetted by Electrolyte

Pore radius $r, \mu\text{m}$	$\log r$	Volumes of Hg ($\text{cm}^3 \text{g}^{-1} \cdot 10^3$) for i (mA cm ⁻²):				
		0 ^a	0	10	30	50
5.6	0.75	0	0	0	0	0
3.12	0.49	33	31	8	17	0
2.16	0.34	63	64	51	47	24
1.67	0.22	93	92	76	96	59
1.35	0.13	129	121	124	123	116
1.13	0.05	162	155	150	146	141
0.913	-0.96	234	230	196	216	208
0.811	-0.90	268	262	230	249	245
0.690	-0.84	321	313	312	312	314
0.5775	-0.76	380	364	365	363	375
0.4640	-0.67	455	424	429	425	446

^aDry electrode.

porous body of the active layer are independent of the cathodic polarization, as was also confirmed by weighing the loaded as well as the unloaded active layers.

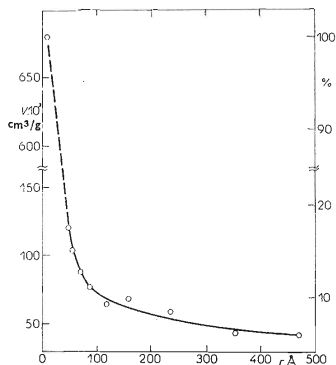


FIG. 5
Volume of Electrolyte V , Referred to 1 g of Active Layer, vs Pore Size r .

The porosimetric measurements gave information regarding the quantity of electrolyte in pores of $r > 0.005 \mu\text{m}$. The quantity of electrolyte found by weighing was constant in all cases and amounted to approximately $0.71 \text{ g } 1\text{M-KOH/g}$ of the active substance. This quantity comprises also the contribution of the electrolyte in the pores which are beyond the possibilities of mercury porosimetry. Fig. 5 gives the results of both methods of measurement. It will be seen from the dependence of the volume of electrolyte on the size of the pores where it is contained that about 90% of the electrolyte is held by pores of $r < 100 \text{ \AA}$, referred to as micropores. The distribution of the electrolyte in the active layer is thus ensured almost exclusively by micropores in the individual carbon grains, whereas the contribution of the transition and macropores is next to negligible.

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