

PLASTIC-BONDED ELECTRODES FOR NICKEL-CADMIUM ACCUMULATORS.

VII. INFLUENCE OF DIFFERENT METAL SCREENS ON THE OXYGEN RECOMBINATION RATE ON PLASTIC-BONDED CADMIUM ELECTRODES

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Summary

The oxygen recombination (reduction) rate on plastic-bonded cadmium electrodes in sealed Ni-Cd systems can be increased by using metal screens applied to the gas side of the plastic-bonded cadmium electrode.

The metal screen applied should have an optimum geometry (mesh size, wire diameter) to provide optimum conditions for the existence of a uniform electrolyte film covering the total screen surface. The oxygen recombination rate in such a case is high enough to enable this type of cadmium electrode to be used in practical sealed cells.

No major differences between steel and nickel screens were noticed, but with a silver plated screen a substantially enhanced oxygen recombination rate was observed.

Introduction

It was shown in the previous paper that the recombination (*i.e.*, reduction) of oxygen at a rate utilizable in sealed Ni-Cd cells takes place on the metal parts of the cadmium electrode which are covered with a thin electrolyte layer easily accessible for oxygen and which are short-circuited with the electroactive material [1]. Therefore, with pocket and sintered type cadmium electrodes the recombination of oxygen takes place mainly on the perforated metal pocket and on the sintered matrix, respectively. In the case of plastic-bonded cadmium (PB-Cd) electrodes [2], these metal parts are missing as the current collector is embedded in the active material and consequently the oxygen recombination rate is too low for the construction of sealed Ni-Cd cells.

We showed [1] that if one or more metal screens are in contact with the gas side (the side facing the gas space of the sealed cell) of PB-Cd electrodes and are covered with an electrolyte film, the recombination rate of

oxygen is significantly enhanced. The aim of the present work was to study the influence of different metal screens and their surfaces on this recombination rate.

Experimental

The positive electrodes were commercial pocket type nickel oxide electrodes of dimensions 4.5×7.5 cm for prismatic sealed Ni-Cd cells. Their capacity was 2.0 - 2.4 A h at the 5 h discharge rate. The negative PB-Cd electrodes were prepared by a rolling technique [2] from a blend of 95 wt.% of powdered active material used in commercial pressed electrodes (essentially cadmium sponge oxidized on the surface in the course of drying) and 5 wt.% Teflon powder (FLUON CD-1, ICI, Great Britain). A steel screen (wire diameter 0.8 mm, mesh size 3.15 mm, mass 2.2 kg/m^2) electroplated with nickel was used as a current collector. The capacity of these electrodes was 2.5 - 3.0 A h at the 5 h discharge rate.

The electrode assembly, the test cell design and the method of electrochemical measurements were described in our previous paper [1]. In some cases an electric tensometer was used simultaneously with a manometer for overpressure measurements.

The specification of the various metal screens applied to the gas side of the PB-Cd electrodes is given below. One or two layers of these screens, of dimensions 4.0×7.5 cm, were used in all cases.

Results and discussion

The measurements were concentrated on the oxygen recombination rate in the presence of different metal screens with different characteristics and chemical composition of the surface layer. The metal screens are specified in Table 1. Screens with a smooth nickel surface were used in most cases, *i.e.*, made either from pure nickel wires (denoted as Ni) or from an iron wire which was galvanically nickel plated (denoted as Fe/Ni). Their geometric structure ranged from 0.05 mm dia. for the finest wire (Ni-0.05) to 0.40 mm for the coarsest wire (Fe-0.4).

TABLE 1
Parameters of applied metal screens

Symbol	Wire diam. (mm)	Mesh size (mm)	Mass (kg/m^2)
Ni-0.05	0.05	0.08	0.29
Ni-0.1	0.10	0.14	0.55
Fe-0.18	0.18	0.71	0.46
Fe-0.4	0.40	1.00	1.48

The dependence of the steady value of oxygen overpressure, Δp , on the charging current for different metal screens, or their combinations, on the gas side of the plastic-bonded cadmium electrodes (in the latter case, the screen contacting the electrode is given first in the description) is shown in Fig. 1. The obvious positive influence of the screens on the recombination rate of oxygen is in accord with the conclusions of our preceding work [1].

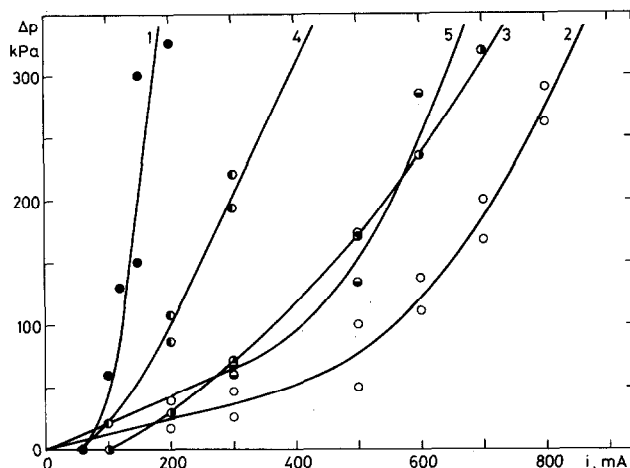


Fig. 1. Influence of the charging current on steady state oxygen overpressure for PB-Cd electrodes with different metal screens on the gas side: 1, without screen; 2, $2 \times \text{Fe-0.18/Ni}$; 3, $\text{Fe-0.18/Ni} + \text{Ni-0.1}$; 4, $\text{Fe-0.18/Ni} + \text{Ni-0.05}$; 5, $1 \times \text{Fe-0.4/Ni}$.

The influence of the geometry of the screens is apparent. Best results were achieved with the combination $2 \times \text{Fe-0.18/Ni}$. If, however, one layer of this screen was combined with a finer one (Ni-0.05 or Ni-0.1), then the oxygen recombination rate was lower. With the combination $\text{Fe-0.18/Ni} + \text{Ni-0.1}$, the corresponding characteristics are identical with those obtained with one layer of the Fe-0.4/Ni screen, which is representative of the coarsest geometric structure.

The results shown in Fig. 1 suggest that the replacement of one of the Fe-0.18/Ni screens with a finer one (Ni-0.05) leads, under the given conditions (elimination of excess electrolyte mode), to the formation of a continuous electrolyte film on the whole screen surface (including meshes), whereby the diffusion of oxygen to the underlying Fe-0.18/Ni screen is hindered. Thus, the recombination rate of oxygen is lowered considerably more than in the case of the combination $\text{Fe-0.18/Ni} + \text{Ni-0.1}$, where the possibility of the formation of a continuous electrolyte film is somewhat smaller.

These findings led us to measure the oxygen recombination rate on a selected screen (Fe-0.4) with varying conditions for the formation of an electrolyte film. This screen has the coarsest geometric structure which practically eliminates the formation of an electrolyte film covering one or more meshes. The conditions for its formation were varied by using either a glossy gal-

vanic nickel plating or a rough nickel layer produced by metallizing techniques; the excess electrolyte adhering to this coarse layer was removed prior to sealing either by blowing with compressed air or by blotting paper. The cell was then assembled and hermetically sealed. For comparison, commercial sintered cadmium electrodes were measured simultaneously, the excess electrolyte being removed prior to sealing either by means of compressed air or by centrifuging. In this case, the content and distribution of the electrolyte in the electrode and on its surface could also be controlled. The results for both PB-Cd and sintered cadmium electrodes are shown in Fig. 2.

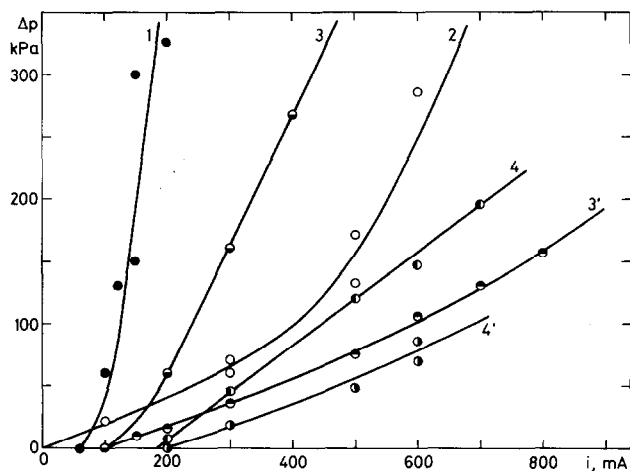


Fig. 2. Influence of the charging current on steady state oxygen overpressure for PB-Cd (1-3') and sintered (4, 4') electrodes. 1, without screen; 2, Fe-0.4/Ni (Ni plating) screen; 3, Fe-0.4/Ni (Ni metallizing) screen; 3', Fe-0.4/Ni (Ni metallizing) screen, electrolyte partially removed; 4, non-centrifuged; 4', centrifuged.

In the case of PB-Cd electrodes with the Fe-0.4/Ni screen, it is seen that the screen with a coarse nickel layer gives rise to the existence of a thick electrolyte film, which is not removed by the action of compressed air and which hinders the transport of oxygen. If a large portion of this adhering electrolyte is removed by the blotting paper, the oxygen recombination rate increases up to the values attained with sintered cadmium electrodes. This is obviously the result of the very thin film of electrolyte on the rough nickel surface of the screen.

With sintered cadmium electrodes, the situation is analogous. If such an electrode is dried by centrifuging, the measured recombination rate after hermetically sealing the cell was higher than with an electrode treated with a stream of compressed air, when the electrolyte layer was thicker.

The dependences of the oxygen reduction rate on the thickness of the electrolyte film on the surface of different metal electrodes which were dipped and then partially drawn out from an alkaline electrolyte [3, 4] support our concept.

With regard to the chemical character of the screen surface, we compared the recombination rate of oxygen using steel (Fe-0.18), galvanically nickel-plated steel (Fe-0.18/Ni), pure nickel (Ni-0.1), and silver-plated nickel (Ni-0.1/Ag) screens. The corresponding characteristics are shown in Fig. 3. It is seen that the oxygen recombination rate in the case of nickel is the same as with steel, but it is much higher in the case of silver owing to its pronounced catalytic properties for the reduction of oxygen [5]. This again supports the electrochemical mechanism for the process. Thus, the PB-Cd electrode with a silver-plated nickel screen proved better from the point of view of oxygen recombination than the sintered nickel electrode (*cf.* Figs. 2 and 3).

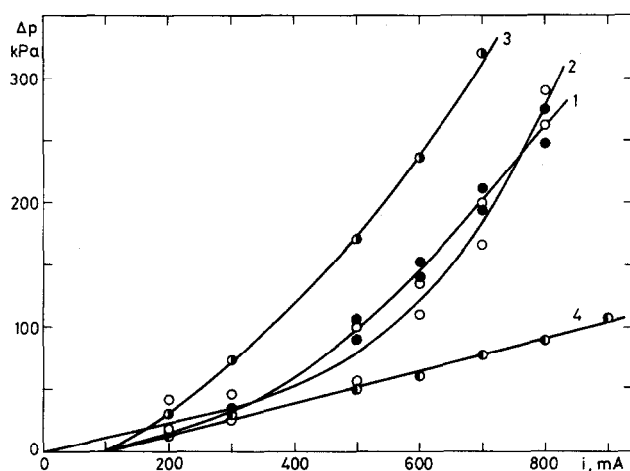


Fig. 3. Influence of the charging current on steady state oxygen overpressure for PB-Cd electrodes with different metal screens on the gas side: 1, 2 \times Fe-0.18; 2, 2 \times Fe-0.18/Ni; 3, Fe-0.18/Ni + Ni-0.1; 4, Fe-0.18/Ni + Ni-0.1/Ag.

The increase in the oxygen recombination rate by the use of metal screens was confirmed generally in the case of sealed Ni-Cd cells where one positive and one or two negative PB-Cd electrodes were used (combination 1 - 1 or 1 - 2). In the case of sealed Ni-Cd cells with a larger number of anodes and cathodes, for construction reasons the metal screens can only be applied to both outer PB-Cd electrodes facing the gas space of the sealed cell. The intense oxygen reduction on them then causes an uneven distribution of the current load on the individual PB-Cd electrodes during charging, overcharging and discharging, which naturally has an effect on the adjoining positive electrodes.

We observed this asymmetry with sealed Ni-Cd cells containing three nickel oxide and four PB-Cd electrodes (combination 3 - 4) (Fig. 4). During advanced charging or overcharging, the flow of electrons is consumed mostly by the outer PB-Cd electrodes (reduction of O_2), hence, the adjoining positive electrodes (outside Ni-ox electrodes — Fig. 4) operate under conditions different from the middle one. This situation leads naturally to an asymmetry during discharging, as demonstrated by the fact that the discharge capacity

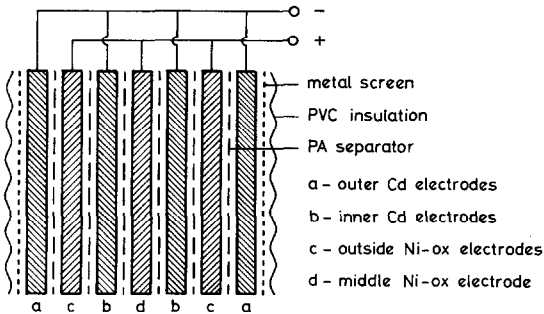


Fig. 4. Electrode arrangement in the cell with the 3 - 4 electrode combination.

drops gradually during cycling to about 65% of the nominal value. Indeed, after dismantling such a sealed cell in the charged state and discharging each positive electrode separately in an excess of electrolyte, the middle nickel electrode always showed a smaller capacity than the other two, outside, electrodes, namely, 25 - 27% of the total capacity of all three electrodes.

By contrast, in the case of a sealed cell with symmetrical recombination (pocket Cd electrodes), all three positive electrodes showed the same capacity, evidence for a symmetrical distribution of the charge among all electrodes in the cell.

The application of the metal screens to the PB-Cd electrodes in sealed Ni-Cd cells can therefore be successful only in the case of the simplest electrode assemblies 1 - 1 or 1 - 2. For systems with a larger number of electrodes, it is necessary to ensure that all the PB-Cd electrodes have an equal recombination capability, and this is the object of our further work.

Conclusions

(1) The oxygen recombination rate on PB-Cd electrodes in sealed Ni-Cd cells is increased by applying 1 or 2 layers of metal screens in contact with the gas side.

(2) The increase in the oxygen recombination rate is especially high if the applied metal screen allows the formation of an electrolyte film on the surface of the individual wires. If its geometric structure is too fine, the electrolyte tends to fill up the meshes with a continuous layer, whereby the oxygen recombination rate drops as a result of a hindrance to the diffusion of oxygen in the electrolyte layer.

(3) Steel and galvanically nickel-plated steel screens result in the same recombination rate. However, galvanically silver-plated nickel screens are much more effective, thus substantiating the electrochemical mechanism of the process.

(4) In the case of PB-Cd electrodes in contact with a screen whose surface is covered with a coarse nickel layer (by metallizing), as well as in the

case of sintered electrodes, the recombination of oxygen was slowed down when the quantity of electrolyte adhering to the screen or to the sintered electrode increased.

(5) The application of 1 or 2 metal screen layers to PB-Cd electrodes was satisfactory in sealed Ni-Cd cells with one positive and one or two negative electrodes. With a larger number of electrodes, where the metal screens can be applied only to the outer negative plates, the asymmetry in the charge distribution among individual electrodes leads to a gradual drop in the cell capacity to considerably below the nominal value.

References

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