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DISCLAIMER

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ABSTRACT

Proof-of-principle experiments are reported for a new concept in electrically rechargeable zinc-air battery. The zinc electrode is a porous flow-thru type using a copper foam metal substrate with zinc deposition onto the foam metal from concentrated zincate electrolyte (as used in zinc-slurry type batteries). The bifunctional air electrode employs low-cost materials, being fabricated entirely from carbon-based precursors and small amounts of nickel and/or cobalt oxide. Corrosion measurements on the graphite materials in the air electrode indicate sufficient corrosion resistance for 8000 hr life on charge. A prototype single cell was constructed having 1.5 Ah capacity producing 1.2 V discharge -2.0 charge at the three hour rate and has produced stable voltages for more than 150 cycles. Based on the 1.5 Ah prototype characteristics, design calculations were made for a 32 kWh battery. These calculations project an energy density of about 110 Wh/kg, peak power density of 140 W/kg, electrical efficiency of 60% and an attractive materials cost of $\lesssim$ \$20 per kWh.

BACKGROUND

As an advanced battery for electric vehicle propulsion, the Zn/NiOOH battery has a number of attractive features: about twice the energy density of lead-acid EV batteries; excellent low-temperature performance; relatively high power density. There are, however, critical technical problems related to cycle life combined with a relatively high materials cost that adversely impact the economic attractiveness of this battery system. The nickel electrode is the principal cost component, while fundamental problems with the alkaline zinc electrode are the principal cycle-life limiting factors.

In this paper, we report the results of proof-of-principle experiments examining two new concepts for an alkaline zinc battery that would have most of the performance advantages of the Zn/NiOOH battery, but would have better cycle life and a significantly lower materials cost. The two new concepts are: i.) a flow-thru porous zinc electrode with recirculating alkaline zincate; ii.) an electrically rechargeable (so-called bifunctional) air electrode based on small quantites of transition metal oxides and a new carbon black. A zinc-air battery with recirculating zincate is not a new concept, as there have been extensive studies of such systems (1). All of these prior systems, however, used an inert electrode with recirculating zinc particles (2) or beads (1,3). What is reported here is the use of a zinc electrode concept derived from the zinc-halogen (acidic electrolyte) battery (4) with materials adapted to the alkaline zincate electrolyte, e.g. use of a much more open-porosity material to accomodate the viscous colloidal electrolyte.

The air electrode incorporates recent developments in new materials for bifunctional air electrodes, in particular, new transition metal catalysts (5) and new corrosion resistant carbons (6), which provide acceptable cell voltage (1.2 V discharge, 2.0 V charge) and cycle life (800-1000 deep discharge cycles) at attractive cost ($\lesssim$ \$20 per kWh).

ZINC ELECTRODE

The zinc electrode concept employed here uses an inert substrate having an open "honeycomb" type porosity onto which zinc is plated and stripped while electrolyte circulates through the open pores. Materials having this type of porous structure are commercially available as either "metal foams" or as "carbon foam". We have studied in some detail the use of copper foam metal, in particular a product obtained from Foametal Inc. (Willoughby, OH). Figure 1 shows a series of electron micrographs of the 10 Pore copper foam metal at different magnification. At low magnification, the open "honeycomb" or retriculated structure is apparent; the nominal honeycomb-cell diameter in this material is 0.2 cm, and the characteristic diameter of the filaments is ca. 0.04 cm (400 μm). At higher magnification, microporosity and roughness on the scale of 1-10 μm is clearly evident. We anticipated that the rough surface of the copper would make an excellent substrate for zinc deposition, and this was in fact observed to be the case. The large cell diameter allows for electrolyte flow through the substrate with a minimum pressure drop, but with a relatively high internal area for zinc deposition. Specifically, the 10 Pore material we used had a bulk density of ca. 3% with a BET

surface area of ca. 10^4 m^2 per m^3 of foam metal. Using a 0.3 cm thick electrode, this results in ca. 30 cm^2 internal area for each cm^2 of superficial area. Thus, the "true" current density for zinc deposition/stripping will be more than an order of magnitude lower than the nominal current density, a factor which should contribute to improved cycle life for the electrode.

Zinc deposition studies were performed in a cell having the same basic geometry as the prototype zinc-air cell shown in Fig. 2, but with the air electrodes replaced with Ni-Exmet® counter electrodes (evolving hydrogen). Three layers of Cellguard® backed with a porous zirconia "cloth" (Zircar ZYW-30A) served as separator, and assured that the electrolyte flowed through the copper foam and not by (around) it. Zinc was deposited from 12 M KOH solution containing varying amounts of silicate and zincate (see later section for details) at various flow rates and current densities. For a given set of conditions, various amounts of zinc were deposited at constant current, with the cell being disassembled and the electrode cross sectioned for analysis of the zinc distribution. A full parametric study of the influence of current density, electrolyte flowrate, and zincate concentration would have involved literally several thousand separate experiments. This was not done; rather, assumptions were made about possible limiting phenomena and some parameters were fixed from battery design considerations. It was assumed that the primary influence of electrolyte flowrate is the variation in zincate concentration in solution as a function of distance from the flow feeder, as represented schematically in Fig. 3. The slope of this concentration profile is proportional to the ratio of the current

density to electrolyte space velocity. It was further assumed that the minimum flow rate required at a given current density is that which avoids having the zincate concentration fall below a critical value at the end-of-charge (resulting in hydrogen evolution instead of zinc deposition in the region near the exit) and also avoids having the zincate concentration exceed the solubility limit at the end-of-discharge (resulting in passivation at the region near the exit). These critical concentrations are not well known, but from the recent study by Foller (1) we estimated that they are 25 g/L and 300 g/L respectively. The current density of interest here is limited by the performance of the air electrodes, which as described below limits the current density range to 1-10 mA/cm^2. Having set the zincate concentrations and current densities, we were able to determine the minimum electrolyte flowrate and the optimum zinc content (mAh/cm^2).

Figure 4 shows a photograph of the zinc deposit on a 0.3 cm thick substrate at a loading of 160 mAh/cm^2, which appeared to be the maximum amount of zincate that could be deposited uniformly within the honeycomb cells. Notice how the zinc deposit mirrors the cell structure of the substrate; although this photograph shows only the external surface, the same type of morphology was seen in cross-section (the foam metal has an isotropic structure). Thicker substrates could hold correspondingly greater amounts of zinc. With the air electrode limiting current densities to about 10 mA/cm^2, the optimum thickness appeared to be about 0.3 cm and the optimum zinc loading to be about 80 mAh/cm^2. The calculated minimum electrolyte flowrate according to the requirements in Fig. 3 is only 0.01 L/hr for a charging current density of 20 mA/cm^2.

Zinc was deposited and stripped from the substrate at constant current conditions of 10 mA/cm^2 and 20 mA/cm^2 to a capacity of 60 mAh/cm^2 using Ni sinter positives (of the Ni-Cd battery type) and the distribution of zinc analyzed at various points in the cycle. At no time in any given cycle did we observe a non-uniform distribution of zinc analyzed at various points in the cycle. Zinc was not completely stripped from the substrate at the end of discharge, even when the electrolyte contained zincate at levels well below the solubility limit, e.g. 25 g/L. If zinc were completely discharged to the point where the electrode potential started to increase from the normal discharge potential of - 1.38 V (vs. Hg/HgO) and evolve hydrogen, analysis of the surface by Auger electron spectroscopy indicated an essentially pure Zn surface layer was still present. A scanning electron micrograph of this surface layer is shown in Fig. 5. The surface layer is a highly porous powder-type structure, with the fine particles being pure Zn. The surface of the underlying substrate appears to be a thin (a few atomic layers) overlayer of Cu-Zn alloy that probably forms in the initial stage of Zn deposition on the first cycle and remains thereafter. Apparently, the "powdery" Zn formed at the end of complete discharge is a "hard-to-strip" state of Zn which is not Cu-Zn alloy, but could be another chemical form, e.g. zinc silicate, aluminate or zirconate. Chemical analysis of the quantity of zinc that could not be stripped at the normal electrode potential was very small, on the order of 1 mAh/cm^2, so this phenomenon did not have a significant effect on the coulombic efficiency.

Because of the scale of the test cell we were using (25 cm^2), and

the relatively large internal volume of the circulating pump, we could not conduct Zn cycling studies in which the zincate concentration in the electrolyte varied to the same extend it would in a real battery, e.g. from 20 g/L at the start of discharge to 200 g/L at the end of discharge. We were able to do cycling tests with a minimum volume of electrolyte equivalent to five times the stoichiometric amount, i.e. a concentration swing from 20 to 55 g/L. To simulate the end-of-cycle conditions, we conducted studies of Zn deposition/stripping at the concentration limits in a practical cell, around 25 g/L (end-of-charge) and around 220 g/L (end-of-discharge). Near ($\pm$ 5 g/L) these limiting concentrations, there appeared to be no problem with Zn distribution or redistribution on cycling, but significantly higher/lower concentrations appeared to be problematic for reasons that are unclear and will require further study. For the preliminary design evaluation, the use of 220 g/L - 20 g/L (170 Ah/g Zn in solution) appeared justifiable on the basis of the cycling tests conducted to date. Further study of this electrode concept with solutions containing higher end-of-discharge concentrations may show that the electrolyte capacity can be increased above this, as the CGE-SAFT work (2) indicated capacities as high as 220 Ah/L are possible.

THE ELECTROLYTE

The electrolyte we used in these studies was the same as that used in the pioneering work at CGE-SAFT (2) with the zinc slurry system, only of course without the zinc powder added. Our initial studies of the electrolyte focussed on the mechanical problems of circulating the

electrolyte through flow manifolds and the foam metal without plugging from the "quasi-colloidal" zincate particles. Using only the silicate "extender" at 25 g/L in 12 M KOH, the maximum zincate concentration we were able to circulate without difficulty in our system was 220 g/L. The electrolyte at this level of zincate was cloudy-white. In our system, we could not circulate the much more concentrated, and obviously colloidal, solutions used by CGE-SAFT and later by Foller (1). The problem appeared to be plugging of the manifold, rather than of the foam metal, so that reengineering the manifold may enable one to use more concentrated electrolytes.

THE AIR ELECTRODES

The air electrodes employed in this study represented a significant departure in approach than used in any of the previous bifunctional electrode technologies, such as that of Westinghouse (7) or of Stockholm (8) for Fe-air batteries. The approach here was to use an all-carbon structure to minimize both cost and weight, and an inexpensive transition metal oxide catalyst of proven stability to maintain low cost. Some sacrifice in air electrode potential may result from such materials restrictions, but as we show in the total system analysis in the next section the performance sacrifice produces a surprisingly modest penalty in energy density and the reduced materials costs results in a much more economical technology.

We established air electrode potential targets from the desired round trip efficiency goal of >60%, or cell voltages of 1.25 V discharge

and 2.0 V on charge. Since the zinc electrode potential is -1.37±0.01 V (vs. Hg/HgO) in either mode, we set the target air potentials at -.13 V on discharge and +0.61 V on charge (vs. Hg/HgO). The goal of air electrode development then is to develop an electrode that will sustain these potentials at the highest possible current densities using materials of acceptable cost and stability.

As a result of several man-years of research at LBL, we have identified two types of carbon-based materials that can be used to form the key structural components of the electrode having the required stability. These two materials are graphite cloth, formed from woven graphite fibers, available from a number of vendors and in our case purchased from Stackpole Carbon; and a proprietary graphite powder having a BET area of ca. 25 m^2g formed by graphitizing heat treatment of an inexpensive carbon precursor. The corrosion resistance of this material with respect to other carbons is discussed in another publication (6). The graphite powder serves two functions: it is impregnated into the graphite cloth to produce the desired porosity to serve as the basic structural element of the electrode; it is impregnated with transition metal oxides to form the active catalyst material.

As catalysts, extensive testing of literally dozens of materials both by LBL and CWRU (5) has isolated two inexpensive oxides having the desired stability, nickel oxide and the anhydrous cobalt spinel oxide (Co_3O_4). Some perovskite materials may also be acceptable according to recent work from ERC (9). Here we used a mixture of cobalt and nickel oxide supported on our proprietary graphite powder using a published preparation procedure (10).

The catalysts and graphite cloth were fabricated into gas diffusion electrodes of a conventional single-layer type by Prototech Company using Teflon (TFE-7C) powder. A Teflon-film backing was applied to the cloth after curing (350^{o}C) using roll-bonding.

Characteristic polarization curves were measured using 1 cm^2 coupons cut from the prototype-size electrode fabricated by Prototech (25 cm^2). The polarization curves were measured in a half-cell apparatus (11) which allowed for accurate IR-correction. As expected, the performance curves were strongly affected by prior treatment of the electrode. Typically, the electrodes are initially very hydrophobic, and the polarization behavior is poor. Reasonable "initial" performance could be realized by starting the electrodes in a charging (oxygen evolution) mode at low current density (1 mA/cm^2) for 100 hr, then a few conditioning cycles at 10 mA/cm^2 (6000 sec per cycle). Characteristic polarization curves for the electrodes after this break-in period are shown in Fig. 6. At the targeted potentials for the air electrode of -0.13 and +0.62 V (vs. Hg/HgO), the sustained current densities with these electrodes can be expected to be ca. 10 mA/cm^2 on discharge and 5 mA/cm^2 on charge. As we show in the system analysis below, these sustained current densities are sufficient to produce a total battery energy density of 90-100 Wh/kg. However, the relatively low limiting current on air (ca. 30 mA/cm^2) with these electrodes produced a disappointing peak power density (60 mW/cm^2). We know from our experience with other gas-diffusion electrodes fabricated from the same catalyst that much higher limiting currents are possible with better electrode structures, e.g. ca. 100 mA/cm^2 has been observed as an air limiting current with the same catalyst. It appears

that the Teflon-film backing was probably too compressed in these electrodes.

THE ZINC-AIR BATTERY SYSTEM

The basic repeating components of the conceptual zinc-air battery were shown in Fig. 2. Two single cells have been fabricated using this design with the zinc electrode, zincate electrolyte, and bifunctional air electrodes described above. The active area in these cells was 25 cm^2. Three layers of Cellguard and the zirconia cloth separator were compressed between the air electrodes and the copper foam metal and to prevent gas bubble formation on the surface of the air electrode during charging. One cell is being cycled at 0.5 A discharge/0.25 A charge to 1.5 Ah, and the second at half that current to 0.75 Ah. The usable capacity of the foam metal in these cells is actually 4 Ah, but a thinner foam metal was not practical and the air electrode limited the usable currents. Both cells are still operational (as of 4/3/86) and have accumulated more than 100 cycles each with cell voltages close to the targets (1.2 V - 2.0 V) and exceptional voltage stability. Battery design calculations and projected performance were made using the characteristics observed on the 1.5 Ah cell.

Battery design calculations were made for a 32 kWh battery delivering 80 A at 100 V at the 4 hr rate. The relatively low current density (10 mA/cm^2) with this technology requires relatively high electrode area to deliver 80 A. Because the basic design is monopolar with edge current collection, the IR losses in the graphite fiber current

collector limit the maximum usable electrode area to ca. 1000 cm^2. Therefore, the 80 A is delivered by four cell stacks in parallel both electrically and mechanically with four independent electric pumps (but a single electrolyte reservoir) and independent manifolds. Possible parasitic shunt currents in the electrolyte manifolds were neglected. Adequate circulation of the zincate electrolyte can be achieved using one 1/20 hp DC electric motor powered pump for each stack. The results of the design calculations based on the performance characteristics of the 1.5 Ah cell are given in Table I.

Performance characteristics of an Advanced Technology battery were projected using different parameters that would reflect improvements in various components. For example, improved air electrodes that sustain higher current density at the same cell voltages were simulated. What these simulations revealed was that this type of battery system has certain "fuel cell" characteristics, in that the system energy density is not very sensitive to the current density. This can be seen qualitatively from the fact that both reactants (zinc and air) are stored external to the cell, and that the system weight is dominated by the electrolyte weight, with the cell hardware constituting a relatively minor part of the total weight. Therefore, the component of the technology which has the greatest impact on the battery is the electrolyte, where simply increasing the zincate capacity of the solution will increase the energy density significantly. The projected characteristics of an Advanced Technology based on increasing the electrolyte capacity to the CGE-SAFT claim of 220 Ah/L and making modest improvements in the air electrode are given in Table II. The

improvements in the air electrode will result in much better power density, and these improvements have already been produced in small electrodes. Projected performance of >100 Wh/kg and >140 W/kg at 60% electrical efficiency seem reasonable based on what has been observed in laboratory-scale study of this battery concept.

In terms of projected performance, the zinc-air flow battery appears to be intermediate between nickel-zinc and iron-air alkaline batteries. However, the zinc-air flow battery should have a significant cost advantage over either competing alkaline technology, and probably better cycle life as well. The principle cost saving comes from the air electrode by eliminating the use of nickel as a structural element and precious metals (e.g. silver) as catalysts. Based on the supplier cost of graphite precursor materials (catalyst support) and vendor costs of graphite cloth (electrode substrate), we project a materials cost for this battery technology of ca. \$20 kWh, a significant cost advantage over nickel-zinc (> \$100 kWh^{-1}) and somewhat less than the Westinghouse claim for iron-air (\$40 kWh^{-1}).

Table I. Characteristics of a 32 kWh Zinc-Air Alkaline Battery Baseline Technology

Design parameters:	1.2 V discharge (4 hr rate) @ 10 mA/cm^2
	2.0 V charge @ 20 mA/cm^2
	60 mW/cm^2 peak power
	170 Ah/ℓ capacity in electrolyte
Electrolyte weight:	250 kg (157 ℓ)
Zinc substrate weight:	28 kg
Air electrode and air manifold weight:	27 kg
Cell frame weight:	15 kg
Pump, reservoir and manifold weight:	16 kg
Air scrubbers:	10 kg (est.)
Total weight:	345 kg (93 Wh/kg) (58 Wh/kg)

Table II. Characteristics of a 32 kWh Zinc-Air Alkaline Battery Advanced Technology

Design parameters:	1.25 V discharge (4 hr rate) @20 mA/cm^2
	1.90 V charge @ 10 mA/cm^2
	120 mW/cm^2 peak power
	220 Ah/ℓ capacity in electrolyte
Electrolyte weight:	200 kg (116 ℓ)
Zinc substrate weight:	26 kg
Air electrode and air manifold weight:	23 kg
Cell frame weight:	15 kg
Pump, reservoir and manifold weight:	16 kg
Air scrubbers:	10 kg (est.)
Total weight:	290 kg (110 Wh/kg) (138 W/kg)

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Fig. 1. Scanning electron micrographs of 10 Pore copper foam metal used as the zinc substrate in the zinc-air flow battery. Increasing magnification from (a) to (c) as indicated in each micrograph.

Fig. 2. Schematic of the repeating components of the zinc-air flow battery: 1.) foam metal substrate for zinc; 2.) EP rubber gaskets; 3.) zirconia cloth separator; 4.) air electrode on a graphite cloth current collector; 5.) polypropylene air flow manifold (bipolar).

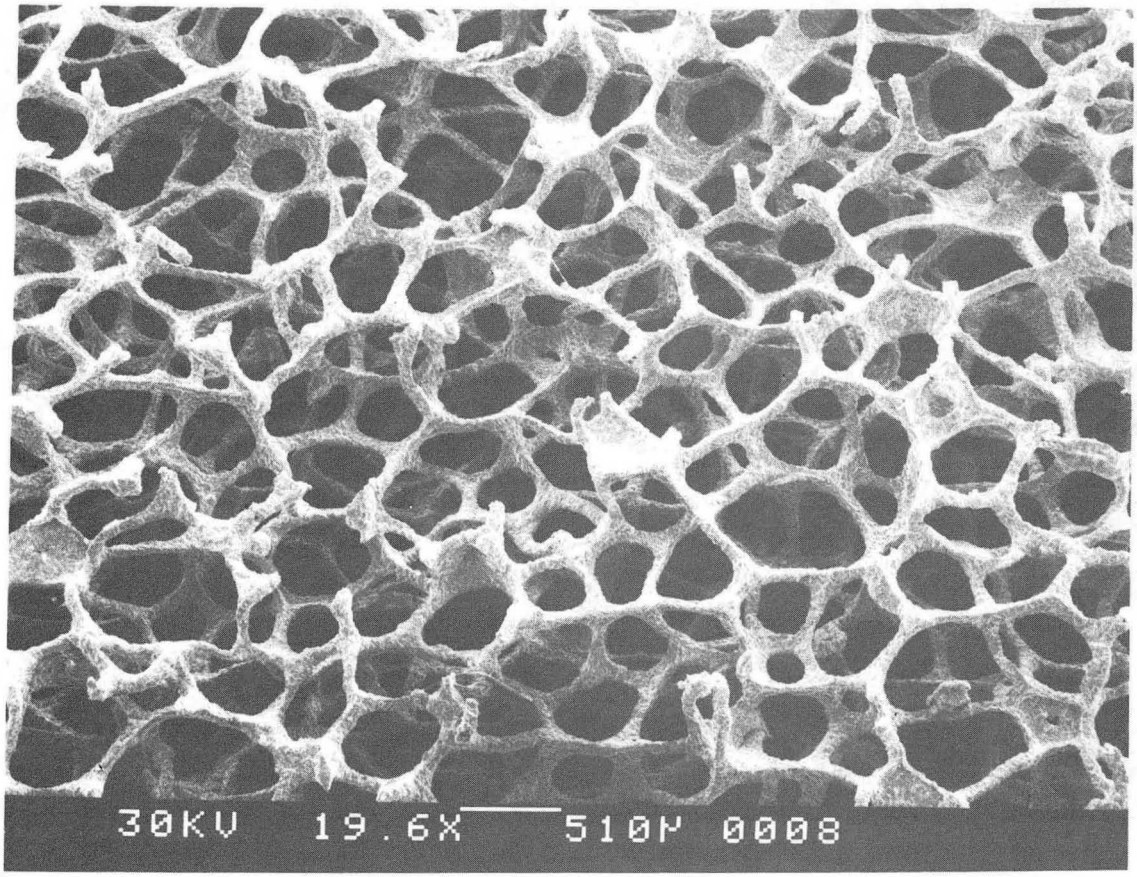
Fig. 3. Concentration profiles for zincate as a function of position in the foam metal substrate at two end-of-cycle conditions. C_2^* represents a critical concentration of zincate for either zinc passivation or hydrogen evolution.

Fig. 4. Optical micrographs of the 10 Pore copper foam metal (a) before and after; (b) zinc deposition of 160 mAh/cm^2.

Fig. 5. Scanning electron micrographs of copper foam metal after an end-of-discharge condition. The electrode had been repeatedly cycled to

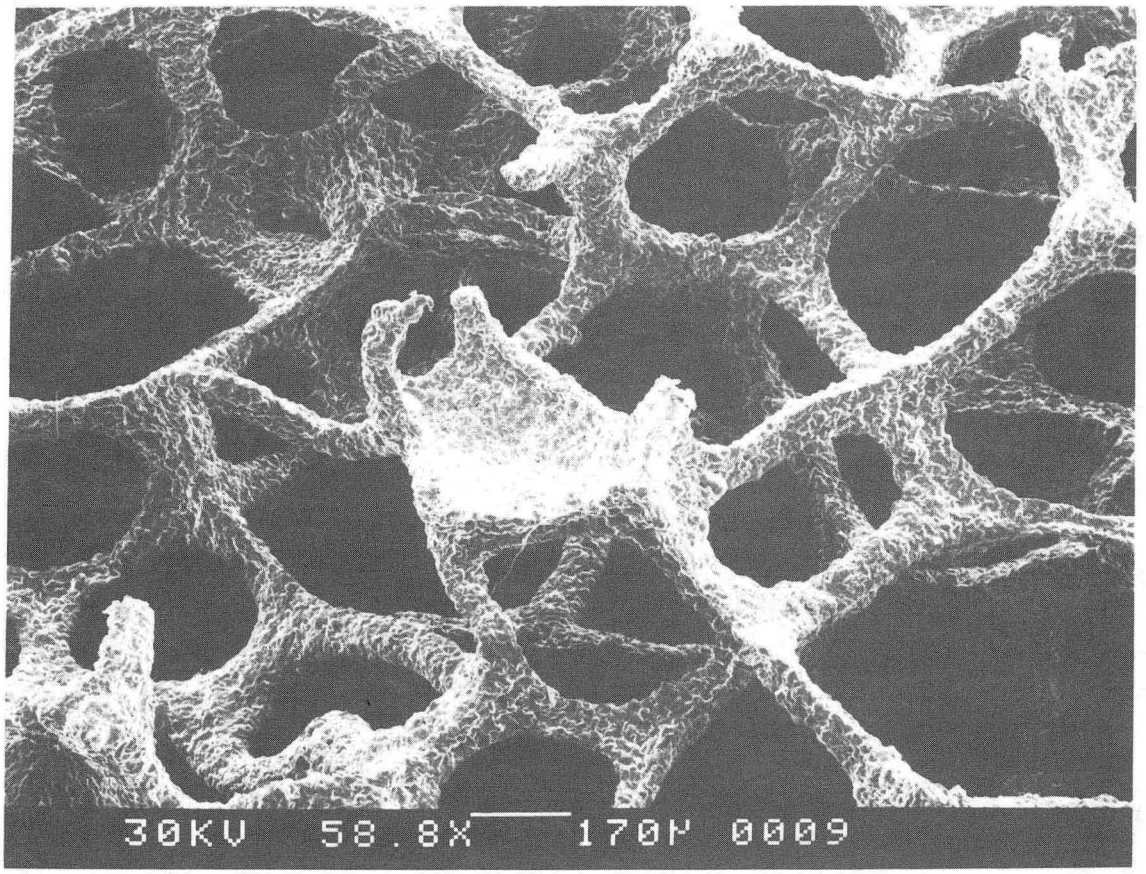
60 mAh/cm^2 prior to this discharge. Magnification is indicated from (a) to (c) on the micrograph. Compare to bare copper substrate in Fig. 1.

Fig. 6. Polarization curves for the 25 cm^2 prototype air electrodes used in the 1.5 Ah cell.



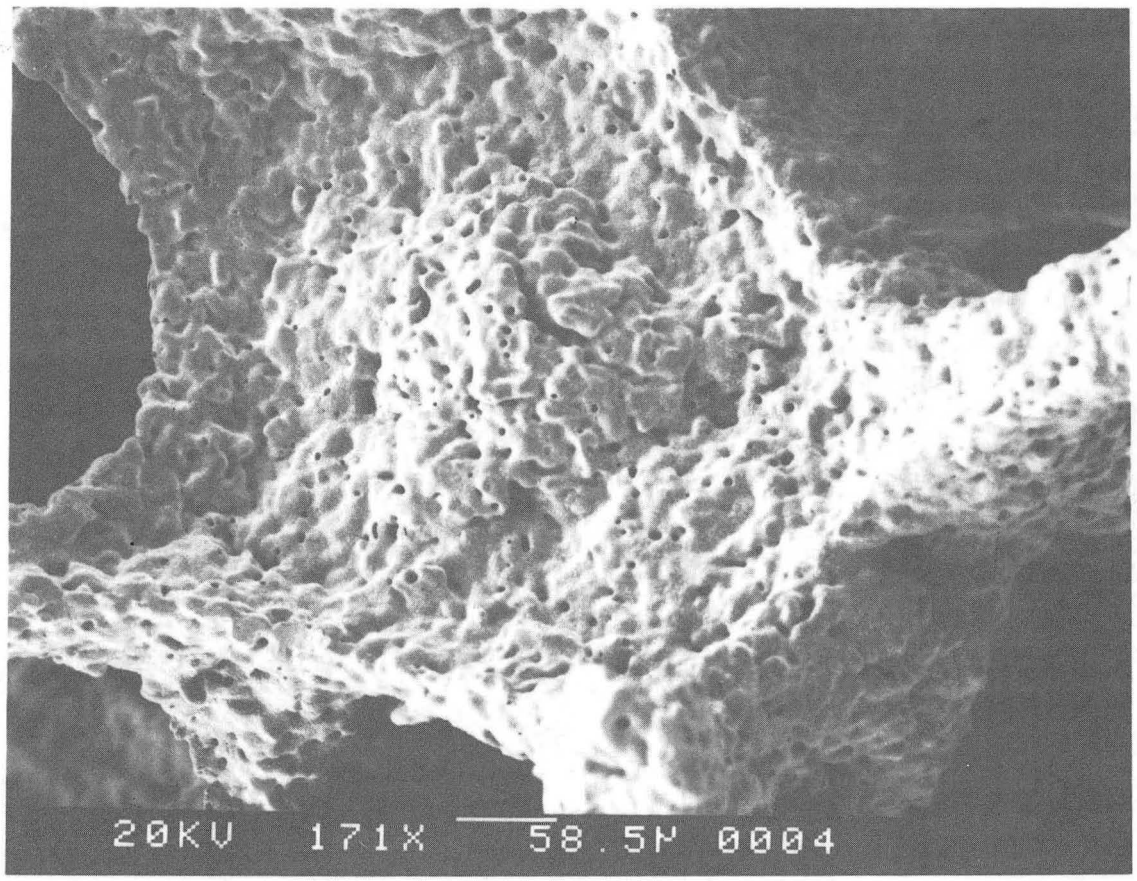
XBB 864-2137

Fig. 1 (a)



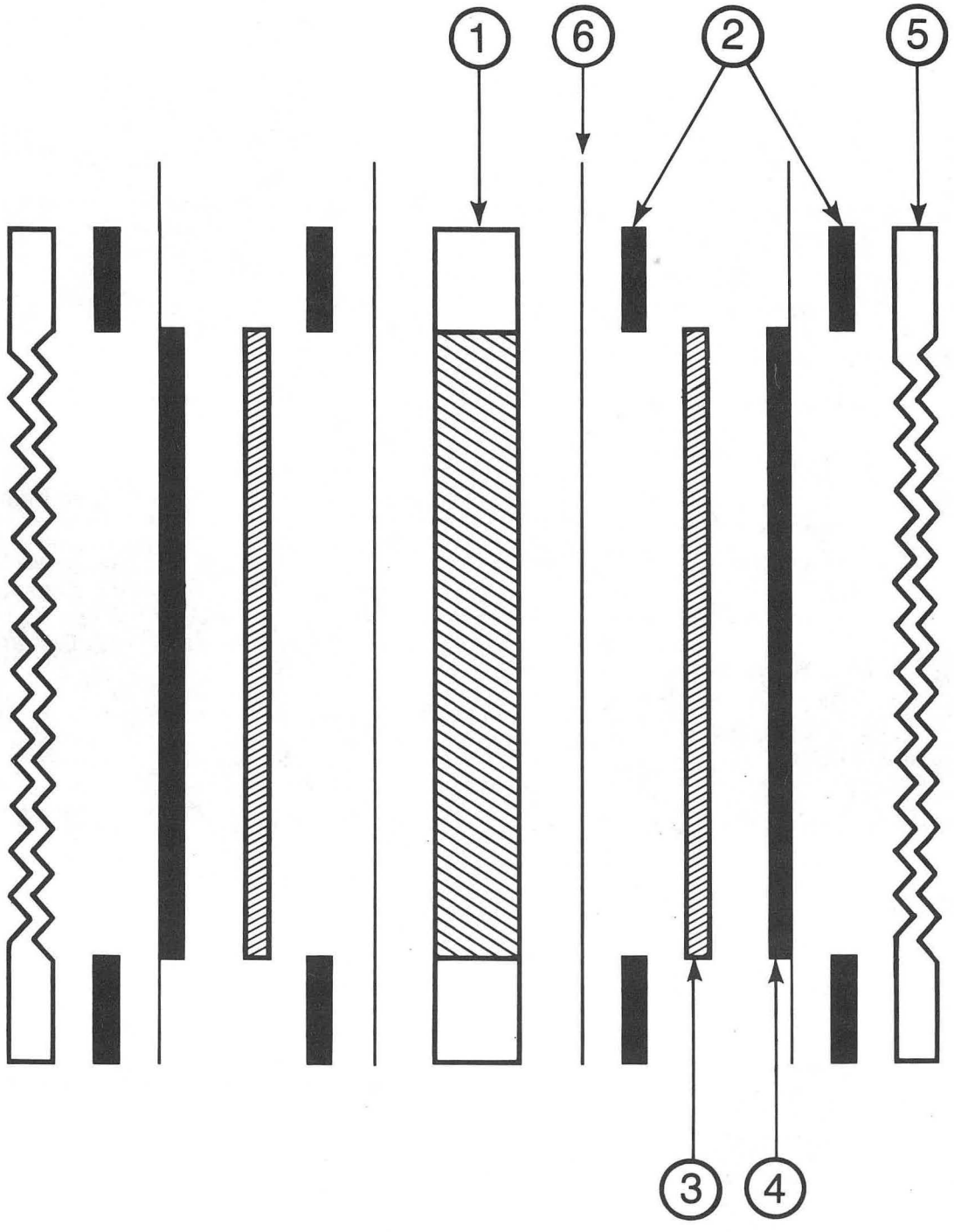
XBB 864-2138

Fig. 1 (b)



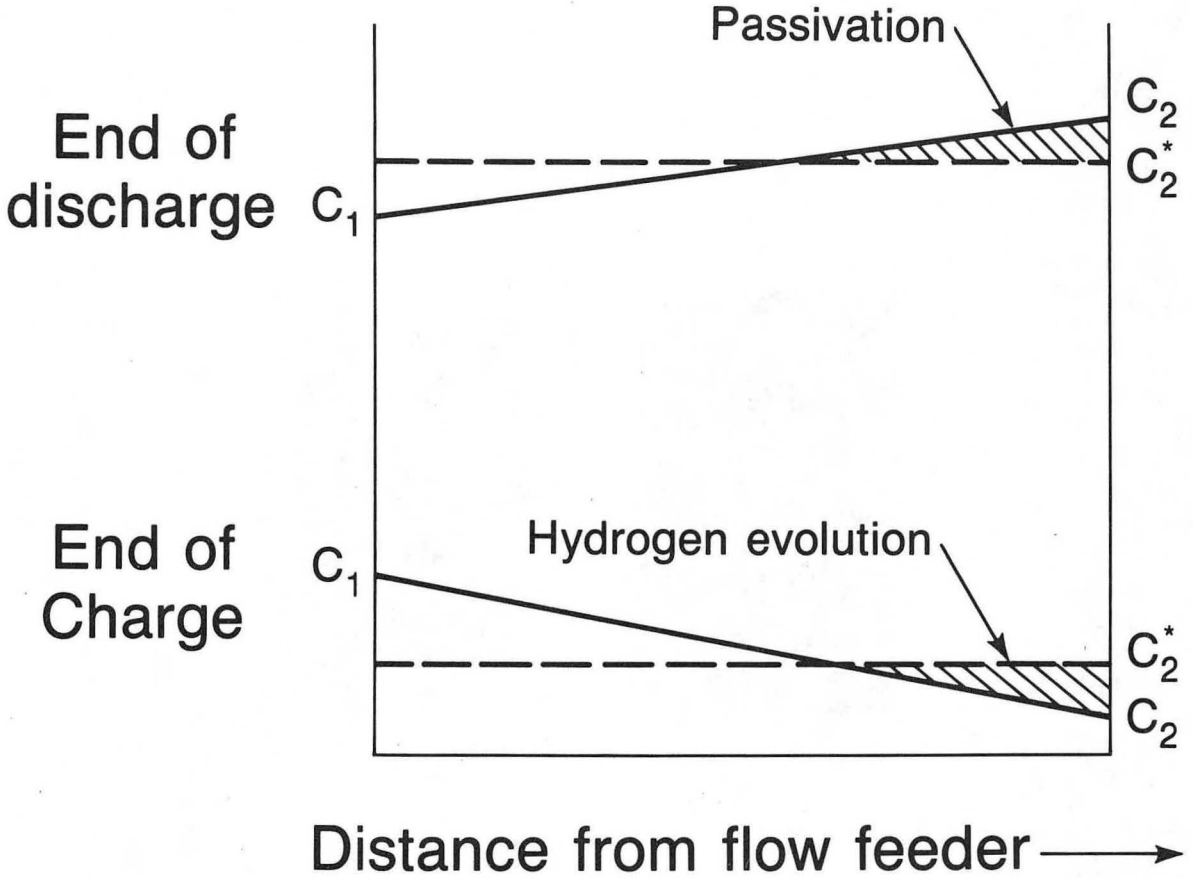
XBB 864-2139

Fig. 1 (c)



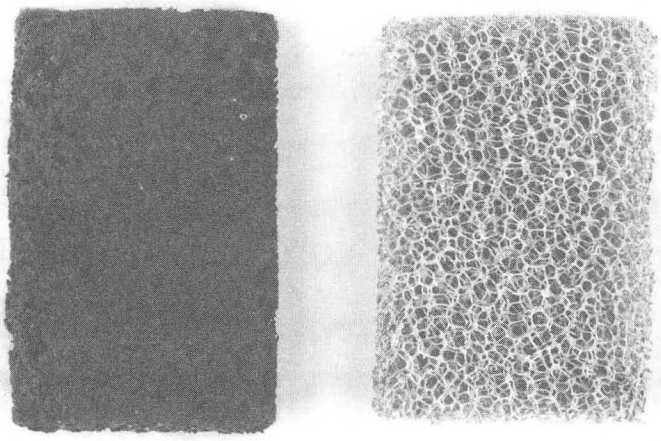
XBL 863-6199

Fig. 2



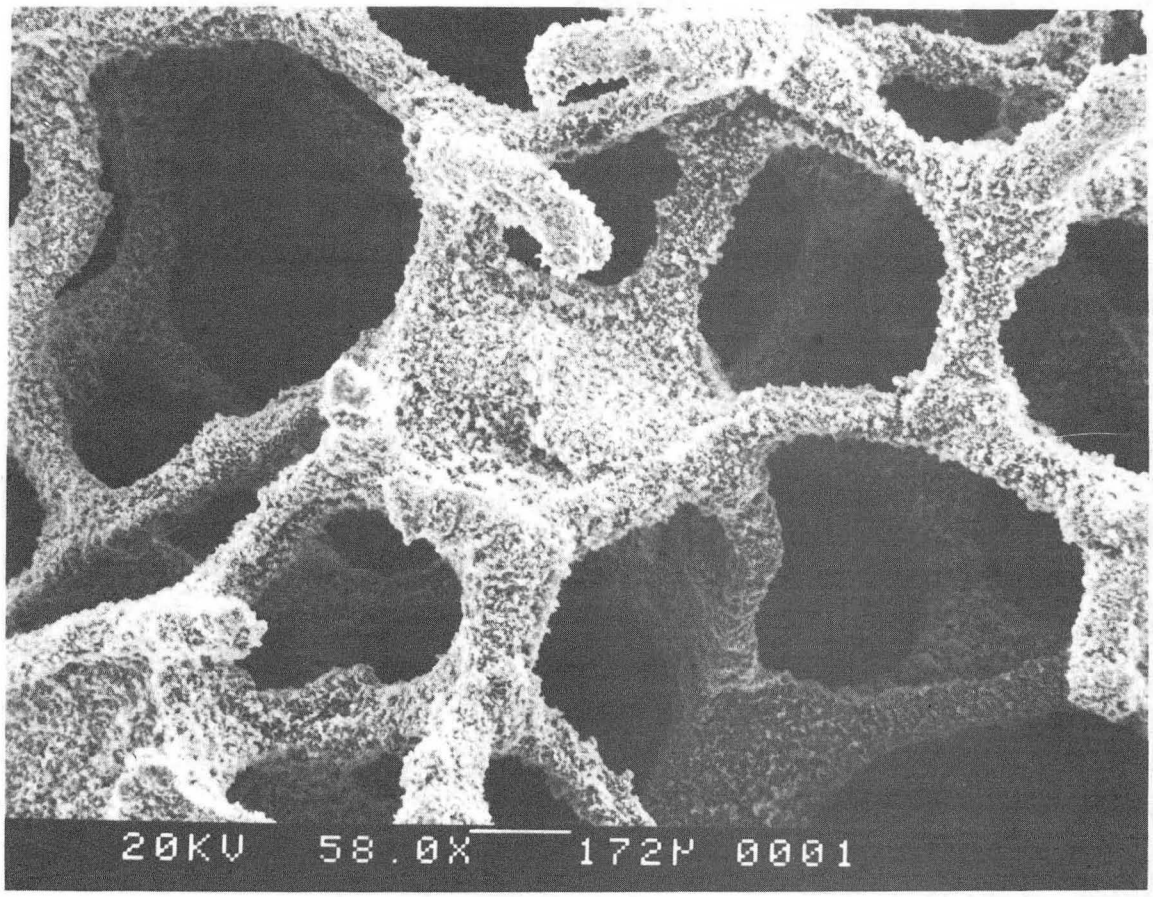
XBL 864-1270

Fig. 3



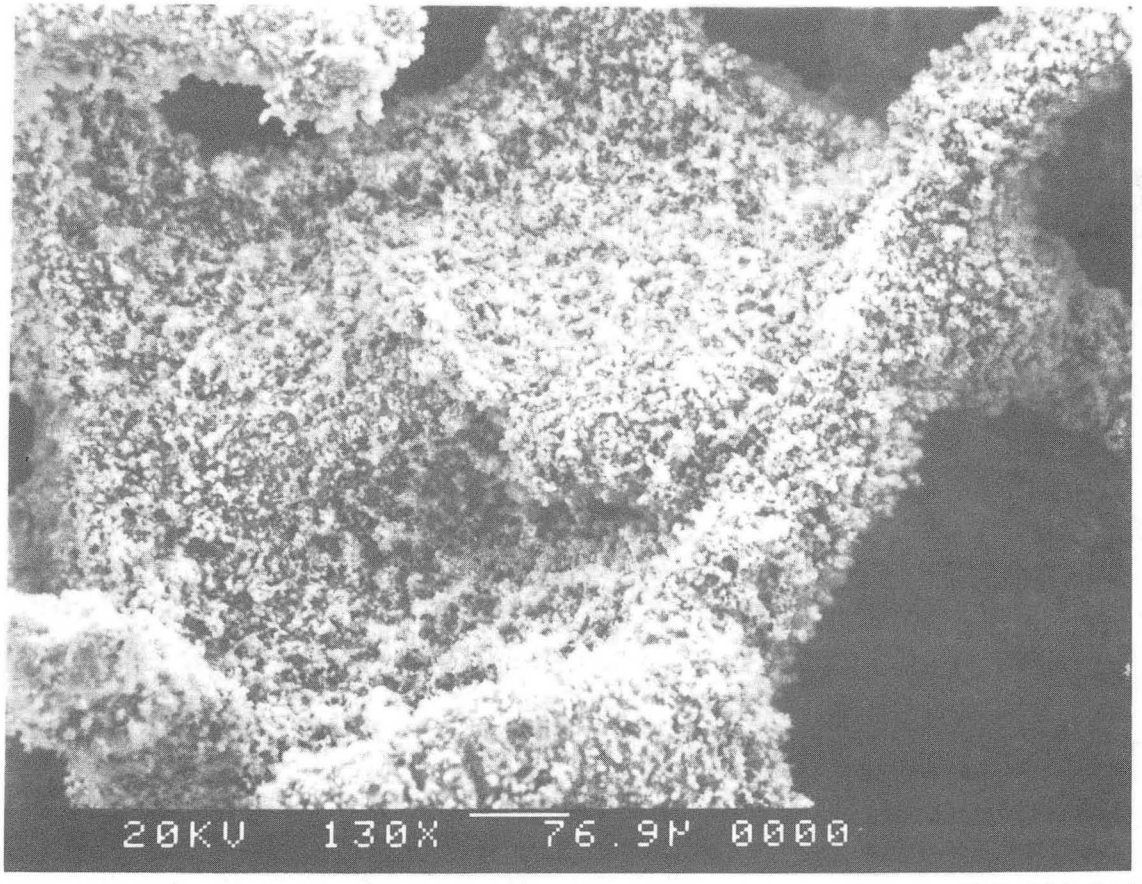
CBB 850-8423

Fig. 4



XBB 864-2140

Fig. 5 (a)



XBB 864-2142

Fig. 5 (b)

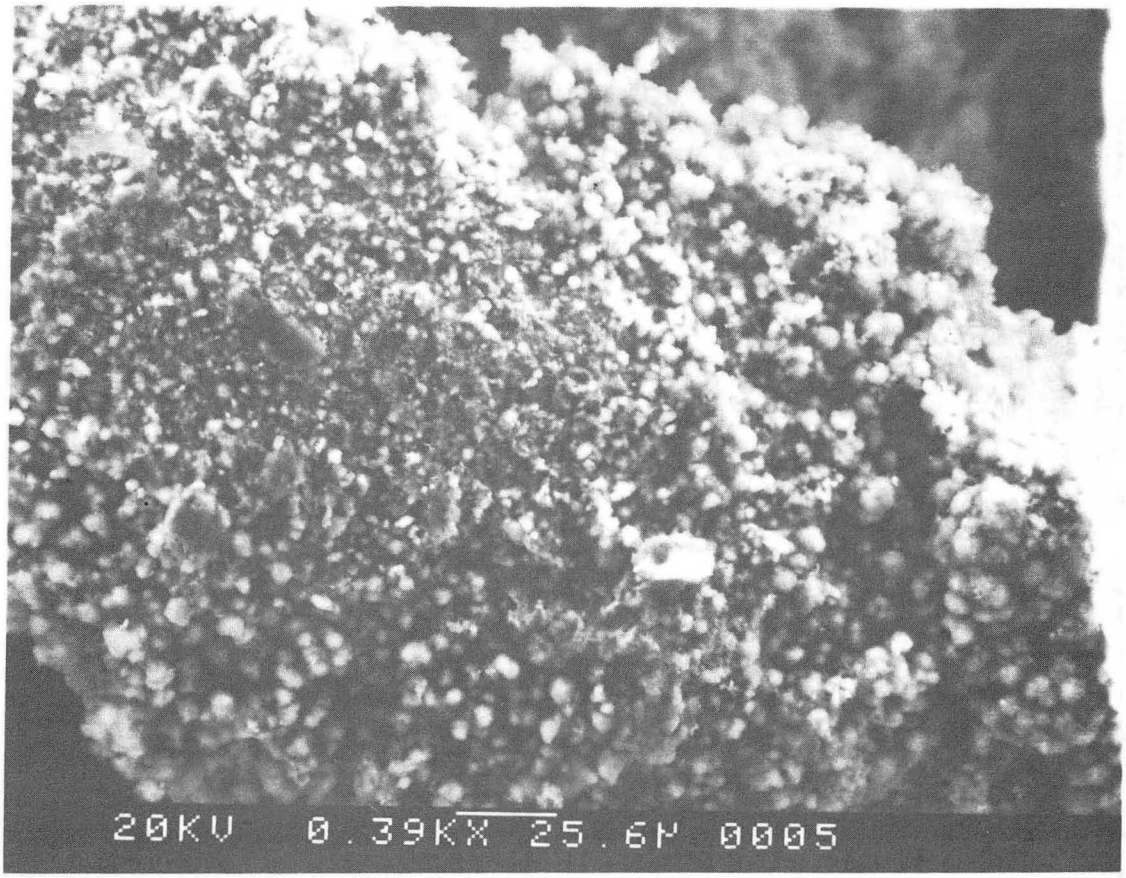


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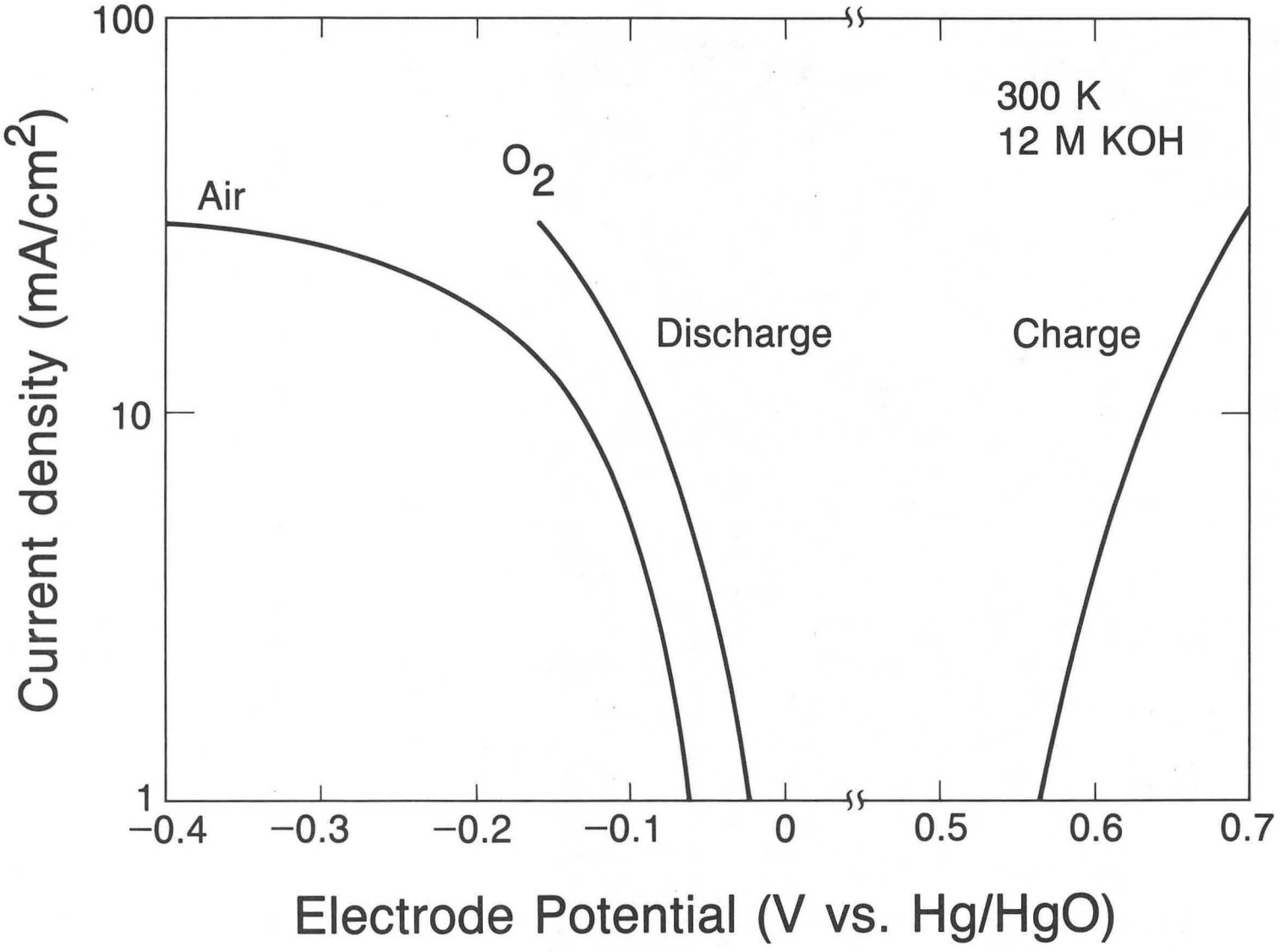
Fig. 5 (c)



XBL 863-6196

Fig. 6

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