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Defining high power EMD through porosimetry

Stuart M. Davis*, William L. Bowden, Thomas C. Richards

Gillette Advanced Technology Center, 37A Street, Needham, MA 02492-9120, USA

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Abstract

High power electrolytic manganese dioxide (HPEMD), offers distinct performance advantages in alkaline-MnO_2 cells compared to the best conventional alkaline EMD materials previously available. Advantages are seen mainly on heavy continuous and heavy pulse drains. No comprehensive model to explain the chemical and structural basis for the improved performance of HPEMD has yet emerged. Hydrothermal electrolytic plating of EMD at 120–125 °C has given rise to several exceptional materials including two samples with excellent high power discharge performance. A systematic study of physico-chemical properties of all of the hydrothermally produced materials as well as commercial EMD samples, including HPEMD, has shown that superior high power performance is linked to porosimetry. By employing the needed plating conditions, one can produce a superior HPEMD material having BET area in the range 20–31 $m^2\,g^{-1}$ and simultaneously a micropore area (deBoer "*t*" method) greater than 8.0 $m^2\,g^{-1}$, all within the context of a typical pore volume of 0.035–0.050 $cm^3\,g^{-1}$ and a calculated meso–macropore radius greater than 32 Å (cylindrical pore model). A qualitative model explaining the need for a balance between BET area and micropore area is proposed. A possible explanation regarding the physico-chemical nature of the micropores and their relation to cation vacancies, as supported by stepped potential electrochemical spectroscopy (SPECS) investigations of heat treated EMDs, is given.

Keywords: Electrolytic manganese dioxide; EMD; High power; HPEMD; Micropores; Porosimetry

1. Introduction

Electrolytic manganese dioxide (EMD) is produced commercially by electrolysis of an aqueous solution of $MnSO_4$ and H_2SO_4. Chemically EMD is a complex inter-growth of the simpler phases pyrolusite and ramsdellite with twin defects, cation vacancies and Mn(III) sites.

This structure is commonly called γ–ε MnO_2 [1] and can be written, following the Ruetschi [2] formalism as:

$$Mn_{(1-x-y)}{}^{4+}Mn_y{}^{3+}\square_x O_{(2-4x-y)}(OH)_{(4x+y)}$$

where $\square$ is a vacancy in the Mn(IV) lattice. In this formula, protons are included to compensate the missing 4^+ charges due to the Mn(IV) vacancies and also the missing 1^+ charge, wherever a Mn(III) replaces an Mn(IV) in the manganese lattice. When $x = y = 0$ (no Mn(IV) vacancies, no Mn(III)), then the formula reduces to stoichiometric MnO_2. When γ–ε MnO_2 (EMD) is heated, protons are lost as water to the extent of 3–6% of the starting weight of the EMD. Physically, EMD is a dense solid with significant internal porosity leading to a high BET surface area (20–100 $m^2\,g^{-1}$). This stands in contrast to other cathode materials such as $LiCoO_2$ (used in Li-ion cells) with BET area of <1 $m^2\,g^{-1}$. Exhaustive investigations have sought to relate EMD battery performance to chemical and crystallographic structure but there has been far less study of the relationship of battery performance to EMD porosity.

HPEMD displays superior performance on heavy continuous and heavy pulse drains to high cut-off voltages. HPEMD can have a significant impact on the high power performance of AA and AAA alkaline batteries. Kerr McGee patent US 6,527,941 B2 [3] describes a process for producing "high power" EMD. According to the teachings of this patent the preferred conditions are: $H_2SO_4/MnSO_4$ ratio = 2:1–4:1 and simultaneously, current density (CD) = 2–4 A ft^{-2}. This

* Corresponding author. Tel.: +1 781 292 8534.
E-mail address: stuart_davis@gillette.com (S.M. Davis).

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may be compared to typical commercial conditions for EMD plating which are: $H_2SO_4/MnSO_4$ ratio = 1:2 and CD = 5–6 A ft^{-2}. The Kerr McGee patent cites improved performance of AA alkaline cells on the 1W continuous drain.

Gillette patent US 6,585,881 B2 [4] describes a process for producing EMD in a pressurized cell at >110 °C. Under particular operating conditions, HPEMD can be obtained. Specific conditions, which have yielded HPEMD are given in Table 1.

Since the high power performance of both the Kerr McGee and Gillette materials are markedly better than ordinary EMD while the conditions under which they were synthesized are markedly different from each other, we may naturally ask what physical or chemical properties these two sets of EMD materials have in common? The purpose of this paper is to compare the physico-chemical properties of these two sets of materials, in particular, those relating to porosimetry, and to show that all other things being equal, what distinguishes a HPEMD from an ordinary EMD is the distribution of surface area between the micropores and the remaining meso–macropores of the EMD.

2. Experimental/materials and methods

Samples of commercial EMD were obtained directly from suppliers or from the IBA (International Battery Association) as "IBA Common Samples". All of these were commercial quality, prepared in high volume production, including two samples of Kerr McGee HPEMD.

The Gillette HPEMD samples, referred to here as EXP1 and EXP27 were prepared at the Gillette Advanced Technology Center, Needham in a hydrothermal electrolytic plating cell of our own design. A description of this cell has been presented at a recent congress [5] and a more detailed description will publish shortly in the full proceedings of the congress (in press). In summary, the plating cell consisted of a Teflon lined pipe spool with total volume of 16.1 l and working volume 11.6 l. Temperature could be adjusted in the range 100–150 °C and maintained to ±0.5 °C. Working pressure was upto 5 atm gauge. With the exception of trial EXP1, the cell was equipped with one Ti anode (two sides + edges = 535 cm^2) and two graphite cathodes (1 side = 355 cm^2). The cell electrolyte was continually refreshed during the plating trial and a constant electrolyte composition was maintained in the cell by balancing the plating current and pump speed. Approximately, 1.5 kg EMD was plated in each trial.

EXP1 constituted a "shakedown" trial for the equipment and different conditions were employed. The Ti anode had an area (2 sides + edges) of 91.1 cm^2 and the two graphite cathodes had an area (one side) of approximately 52 cm^2 Electrolyte was static and the quoted composition was the average for the 10-day trial, varying by ±15% around the nominal values. The key operating conditions for EXP1 and EXP27 are given above in Table 1, Section 1.

Electrolytic solutions were prepared with reagent $MnSO_4{\cdot}H_2O$ (Spectrum, ACS, M1115), reagent H_2SO_4 (Fisher, ACS, A300-212) and de-ionized H_2O. Final pH was adjusted as needed by small additions of $MnCO_3$ (Spectrum, ACS, M1100) or H_2SO_4. After pH adjustment the solutions were clarified by addition of small quantities of reagent H_2O_2 (Alfa Aesar, ACS, stock no. 33323).

The cell was filled with electrolyte having the desired operating composition. For all trials where circulating electrolyte was employed (EXP1 excepted) the pumping speed for the feed solution was balanced against the electrolysis current so as to maintain a constant composition within the cell. The manganese concentration in the feed solution was arbitrarily set at 150% of that for the cell electrolyte so that with a 33% stripping ratio, the desired manganese composition was maintained. The H_2SO_4 level in the feed was adjusted so that with 33% Mn stripping from the feed, the final desired level of acid was generated in the cell. Quality checks on the feed and effluent solutions consisted of regular monitoring for density, pH and conductivity using a glass hydrometer float, a Fisher Accumet pH meter (model 15) and a GLI International inductive conductivity probe (model 33, Cole Parmer cat. no. 19065-34). Two of these 3 variables are sufficient to define a unique composition of $H_2SO_4 + MnSO_4 + H_2O$. Through the use of previously constructed contour plots for paired variables we were able to conveniently monitor the H_2SO_4 and $MnSO_4$ levels and to cross check values obtained from one plot (e.g. density, conductivity) against another (e.g. density, pH). In the event that the effluent composition showed any sign of drifting, the pump speed was adjusted to bring it back to the desired values.

The EMD samples were "finished" by the conventional procedure of crushing in a steel jaw crusher, grinding in a steel "Shatterbox", water washing and neutralizing with NaOH to a constant pH of 5.0–6.0. Drying was done at 60 °C for 24 h in a forced convection oven with the powder contained in a glass tray. The maximum powder thickness was limited to 1.3 cm to insure easy escape of sorbed water. The powder cake was turned over once or twice during drying. (Temperature was limited to 60 °C in order to avoid any possible degradation of the EMD due to overheating.)

Porosimetry measurements were made on a Quantachrome 6 station Autosorb unit with N_2 gas. Prior to

Table 1
Plating conditions for two high power EMD samples in a pressurized cell

Trial	H_2SO_4 (M)	$MnSO_4$ (M)	$H_2SO_4/MnSO_4$ (ratio)	CD (A ft^{-2})	Temperature (°C)	Other
EXP1	0.63	0.88	0.72	6.19	120	Ti doped
EXP27	1.04	0.75	1.39	9.38	120	None