Preparation of Mn-Pb Mixed Oxide Electrode and its Discharge-Recharge Characteristics

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It has been found that an application of electrolytic manganese dioxide (EMD) production technology would create a new rechargeable cathode active material composed of a mixed oxide of manganese and lead.

In order to investigate the possibility of electrolytic manganese dioxide doping of the PbO_2 particles, a quantity of PbO_2 powder was pasted with a small amount of sulfuric acid onto a lead sheet and dried. Then, the PbO_2-coated lead sheet was provided to electrolysis using this sheet as a positive electrode which was placed in between the two lead sheets, which served as negative electrodes. The electrolysis was carried out in a mixture solution of sulfuric acid and a pre-determined amount of manganese sulfate, so as to anodically oxidize the Mn(II) ions present and to precipitate EMD into or around the PbO_2 particles. Figure 1 shows the experimental setup of the electrolysis, where a 3-liter beaker was used as the electrolysis cell. The bath temperature was maintained at 92-95ºC, in a manner similar to the actual EMD production, by means of an electric mantle heater in this case.

Discharge tests were successively conducted by using the electrolysis device (Fig. 1) as the electrochemical cell per se. Figure 2 shows typical examples of charge (Fig.2-(a)) and discharge (Fig.2-(b)) curves. The discharge curves obtained featured a very gradual reduction in potential with a longer discharge duration from the initial working voltage of about 2 V down to an end voltage of 1.3 V. On the other hand, the plain PbO_2 electrode without the EMD doping showed a sudden potential drop (Fig.2-(c)), as in the same manner as a usual lead acid battery, showing approximately one half discharge duration. A considerable charge-discharge recyclability was obtained.

The new aqueous secondary battery was capable of discharging at an elevated temperature as well as room temperature, and the battery performance in the former case was better than in the latter.

It is interesting to note that the EPMA examination revealed that the three micro-domains of; PbO_2, MnO_2, and $Pb_{1-x}Mn_xO_2$, settled together in a thick mixture in the battery active layer on the positive electrode surface. Figure 3 is a schematic representation of aggregate of the three micro-domains. The x-value of $Pb_{1-x}Mn_xO_2$ was calculated to be 0.6 - 0.7, based on the PbO_2 used and on the manganese sulfate added. The assumption made here was that the lead and manganese were uniformly distributed after the synthesis. It may be worthy of pointing out that the $Pb_{1-x}Mn_xO_2$ signifies that the manganese ions are introduced into the PbO_2 crystal lattice. The thermo-analyses and the X-ray diffraction patterns obtained with the Mn-Pb mixed oxide species were different from those of the individual PbO_2 and EMD samples.

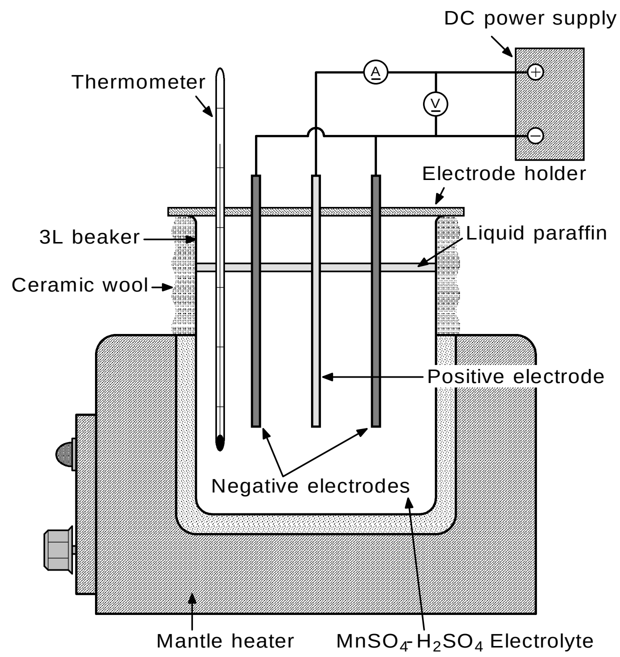

Fig. 1 Experimental setup for electrolysis (charge), and discharge tests of Mn-Pb mixed oxide electrode (positive).

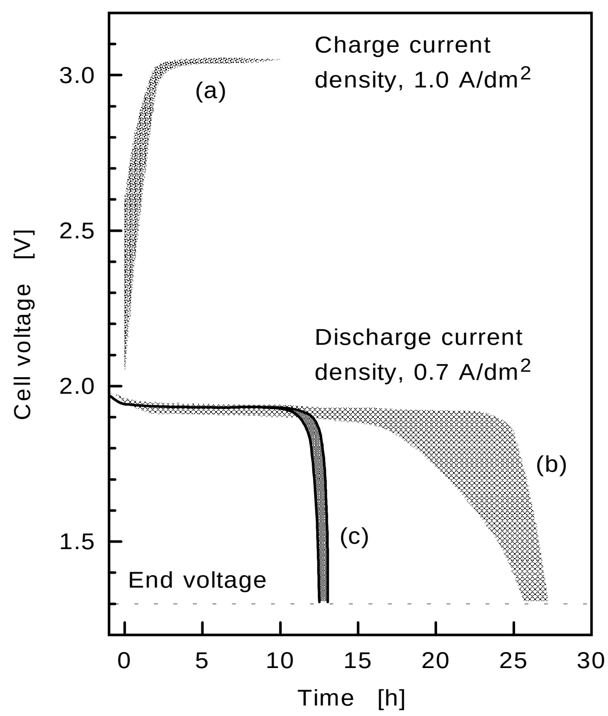

Fig. 2 Typical examples of charge (a) and discharge (b) curves at 92-95ºC. Positive electrode, Mn-Pb mixed oxides mounted on a Pb plate; negative electrode, two plain plates; electrolyte, a hot aqueous H_2SO_4 solution. Corresponding Pb-acid battery showed a discharge curve (c).

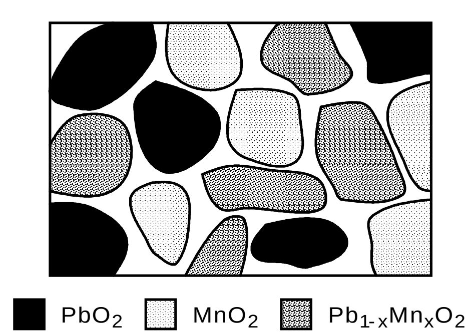

Fig. 3 Schematic representation of microstructure of Mn-Pb mixed oxide materials obtained.