Surface propertie of alkaline batteries active manganese dioxides.

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The most active forms of MnO_2 used as cathode material in primary alkaline batteries are the synthetic and disordered γ/εMD. The structural disorder, necessary to a good electrochemical activity, is described by two types of defects, which affect the orthorhombic network of ramsdellite (fig.1): Pr, a random intergrowth of tetragonal pyrolusite blocks and Tw: microtwinning of this interspersed structure[1]. Both parameters quantify the electrochemical activity of these synthetic MD [2]. Relationships between lattice para-meters of γ/εMD having increasing percentage of structural defects and their surface properties at the gas and liquid interface were investigated.

Low pressure gas adsorption isotherms of N_2, Ar and H_2O vapor lead to characterize the heterogeneity of surface energy [3]. Analysis of water adsorption isotherms showed that the cross sectional surface area of water molecules is linearly correlated to Pr : 6.3 $\mathring{A}^2$ for ramsdellite and 13.1 $\mathring{A}^2$ for pyrolusite. N_2 and Ar isotherms evidenced a correlation between high energy sites and Tw (fig.3). Titration of the surface charge of pyrolusite, ramsdellite and well characterized γ/ε-MD, evidenced a linear relationship between PZC and Pr starting from ramsdellite (Pr = 0, Tw = 0, PZC = 1) to pyrolusite (Pr = 1, Tw = 0, PZC = 7.3). γ/ε-MD with intermediate values of Pr (0.2 to 0.45) have increasing PZC values (fig. 2). For similar Pr values, high Tw percentage (0.3 and 1) makes PZC to increase. The surface charge density is determined from the titration curves and BET isotherms measurements.

Fig. 2 : Variation of the Point of Zero Charge of γ-MnO_2 with Pr.

Fig.3 Low pressure N2 isotherm adsorption evidences high energy sites on EMD Tc in using the Derivative Isotherm Summation (DIS) method.

References
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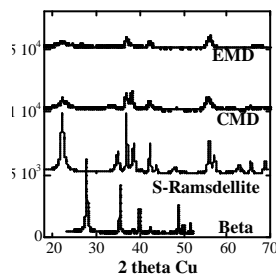[3] Villiéras, F., Cases, J.M., François, M., Michot, L., Thomas, F. *Langmuir* **8** 1789 (1992).

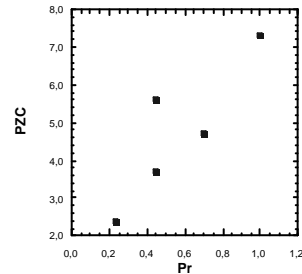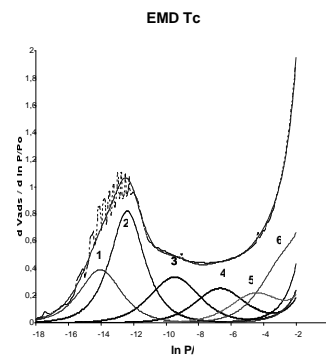Fig1 : XRD pattern of γ-MnO_2 with increasing rate of defects