

## Outer and Inner Surface Contribution in Manganese Dioxides Energy Storage Characterization by Cavity Microelectrode Technique

Laurence Athouël<sup>a</sup>, Paul Arcidiacono<sup>a</sup>, Claudia Ramirez-Castro<sup>a</sup>, Olivier Crosnier<sup>a</sup>, Daniel Guay<sup>b</sup>, Daniel Bélanger<sup>c</sup>, Thierry Brousse<sup>a</sup>

<sup>a</sup> IMN-ST2E, Institut des Matériaux Jean Rouxel, UMR-CNRS 6502, Université de Nantes, Site de la Chantrerie, rue Christian Pauc, BP 50609, 44306 Nantes Cedex

<sup>b</sup> INRS, EMT, CP 1020, Varennes, Québec, J3X 1S2, Canada

<sup>c</sup> UQAM, Département de Chimie, CP 8888, Montréal Québec, H3C 3P8, Canada

Crystallized manganese dioxides powders (cryptomelane type  $\alpha$ -MnO<sub>2</sub> and birnessite type  $\delta$ -MnO<sub>2</sub>) have been electrochemically investigated in mild aqueous electrolytes with the cavity microelectrode (CME) technique [1]. MnO<sub>2</sub> has been widely investigated since many years for its performance as electrode materials for electrochemical capacitors [2]. The microelectrochemistry on small quantities of powder makes it possible the study of active materials for batteries and supercapacitors, without the use of an electronic conductor and a binder [3], as in a composite electrode [4]. The microcavity (10<sup>-3</sup> mm<sup>3</sup>) ensures the characterization of a few hundred nanograms of the pristine isolated MnO<sub>2</sub> powder, making possible a kinetic approach with a bigger range of cycling rates, in particular reachable high cycling rates, as many hundred mV per second.

The use of the CME technique has been previously investigated to characterize electrochemically these manganese dioxides (cryptomelane-type  $\alpha$ -MnO<sub>2</sub> and birnessite-type  $\delta$ -MnO<sub>2</sub>), allowing the access to a small reactive volume and then high kinetic studies [1]. This technique has been proved to be a good way to perform successfully the pseudocapacitive behaviour of powder micro quantities of these active materials used for electrochemical capacitors.

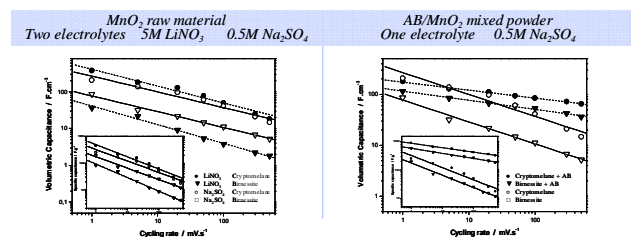


Figure 1: Volumetric capacitance per cm<sup>3</sup> of cavity (insert specific capacitance per gram of active material) versus the cycling rate from 1 mV/s to 500 mV/s (cycle #3)

The role and the need of the acetylene black (AB) conductive part without the influence of the binder, commonly used in a composite electrode, have been consequently highlighted (figure 1), showing its importance in the surface accessibility of the active material at high cycling rate, whereas the bulk diffusion of cations is predominant at low cycling rate [1]. In order to highlight these evolutions, the voltammetric charge  $q$  as well as its reciprocal  $q^{-1}$  is plotted as a function of  $v^{-1/2}$  and  $v^{+1/2}$ , respectively for both volumetric and specific charges. This allows evidencing the  $q_{\text{outer}}$  and  $q_{\text{inner}}$  charges related to the more accessible and less accessible

regions of the surface during cycling, respectively [6], as reported in the following table.

		C.cm <sup>-3</sup>		C.g <sup>-1</sup>		
		$q_{\text{outer}}$	$q_{\text{inner}}$	$q_{\text{outer}}$	$q_{\text{inner}}$	
$\alpha$ -MnO <sub>2</sub>	5M LiNO <sub>3</sub>	40	544 ± 78 (14%)	48	685 ± 85 (12%)	
	0.5M Na <sub>2</sub> SO <sub>4</sub>	without AB	56	230 ± 42 (18%)	68	289 ± 50 (17%)
		with AB	77	88 ± 14 (16%)	386	424 ± 66 (16%)
$\delta$ -MnO <sub>2</sub>	5M LiNO <sub>3</sub>	0.8	812 ± 110 (14%)	1.9	1694 ± 236 (14%)	
	0.5M Na <sub>2</sub> SO <sub>4</sub>	without AB	1.4	117 ± 16 (14%)	3.3	269 ± 40 (15%)
		with AB	47	58 ± 7 (12%)	235	302 ± 35 (12%)

$$q_{\text{total}} = q_{\text{outer}} + q_{\text{inner}}$$

Total voltammetric charge
Surface accessibility
Inner region accessibility

These results mean that at high cycling rate the surface pseudocapacitive process (EDLC and redox reactions) requires acetylene black incorporation to enhance the electronic conductivity of the active electrode material and then its surface accessibility. On the other hand, at low cycling rate the effect of the electronic conductivity is finally not the primary reason of the electrochemical performance. The ionic conductivity plays a major role, since with or without acetylene black the cations intercalation and then the diffusion through the material bulk are mainly evidenced. All these results are however significant of an increase of the kinetic of the pseudocapacitive process in manganese dioxides, due to the high electronic conductivity of acetylene black. Also other parameters, as well as the ionic conductivity in the materials bulk associated to the microstructure or the effect of the potential diffusion can influence the charge storage mechanism in MnO<sub>2</sub>, as illustrated in the literature [7] and more recently by modelling MnO<sub>2</sub> pseudocapacitive behavior [8]. The ionic size of the cation plays also a major role in the electrochemical performance, showing a less surface accessibility and diffusion through the material bulk when the hydrated ion size is higher.

**Acknowledgments:** The authors thank the French National Research Agency (FlexCap project) for financial support

### References

- (1) L. Athouël, P. Arcidiacono, C. Ramirez-Castro, O. Crosnier, C. Hamel, Y. Dandeville, P. Guillemet, Y. Scudeller, D. Guay, D. Bélanger, T. Brousse, *Electrochimica Acta*, 86 (2012) 268
- (2) D. Bélanger, T. Brousse, J. W. Long, *Electrochem. Soc. Interface* 17 (2008) 49
- (3) V. Vivier, Réseau UMEC, *Microélectrode à cavité : principe, développement et applications*, Publications de l'Université Jean Monnet de Saint-Etienne (2009)
- (4) L. Athouël, F. Moser, R. Gugas, O. Crosnier, D. Bélanger, T. Brousse, *J. Phys. Chem C* 112 (2008) 7270
- (5) V. Vivier, S. Belair, C. Cachet-Vivier, J.Y. Nédélec, L.T. Yu, *J. Power Sources* 103 (2001) 61
- (6) S. Ardizzone, G. Fregonara, S. Trasatti, *Electrochimica Acta* 35 (1990) 263
- (7) O. Ghodbane, J.L. Pascal, F. Favier, *ACS Appl. Mater. Interfaces* 1 (2009) 1130
- (8) P. Guillemet, T. Brousse, O. Crosnier, Y. Dandeville, L. Athouël, Y. Scudeller, *Electrochimica Acta* 67 (2012) 41