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A synchrotron X-ray powder diffraction and step potential electrochemical spectroscopy study on the change in manganese dioxide capacitive behaviour during cycling

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ABSTRACT

In this work, the factors leading to the overall capacitance of manganese dioxide electrochemical capacitor materials, i.e. the double layer and pseudocapacitive behaviour, have been separated using Step Potential Electrochemical Spectroscopy (SPECS). In addition, variations in these parameters have been linked to regions of structural change in the material. In regions where ion diffusion into the bulk of a material is a facile process, the pseudocapacitive charge storage shows an increase. In addition, the double layer capacitance has been shown to increase with reduced protonation of the material surface. This has been attributed to variations in electronic resistance and also an increase in the number of sites that can accommodate electrostatic charge. Further, the origin of the residual current seen in previous experiments has been determined. In structures where ion diffusion into the bulk is a facile process, the residual currents are related to this process. Where there is no bulk ion diffusion, the residual currents have been assigned to the production of soluble Mn^{2+} .

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1. Introduction

Electrochemical capacitors, often called supercapacitors or ultracapacitors, are electrochemical energy storage devices capable of high power output over many thousands of cycles. They store energy via charge separation in an electrochemical double layer, and via fast reversible redox reactions occurring at the electrode-electrolyte interface. The contribution from each of these processes varies, with some materials (e.g. activated carbons) obtaining most of their capacitance from double layer effects, while other materials (e.g. conductive polymers and metal oxides) obtain varying degrees of capacitance from each process depending on the nature of the material [1].

Electrochemical capacitor electrodes are commonly made from carbon (including but not limited to graphene and activated carbon), conducting polymers (such as polypyrrole) and metal oxides

(such as manganese dioxide and ruthenium dioxide). The most desirable materials are those which are highly active in terms of gravimetric charge storage, and which can maintain high activity over a large number of cycles. Additional properties of interest include low cost and low toxicity.

Manganese oxides are promising materials for electrochemical capacitors as they show a high degree of pseudocapacitive activity and readily tuneable morphology, with a large number of crystal phases available, each with varying structural locations into which cations can intercalate, the products of which have differing energies of formation and therefore different electrochemical potentials associated for intercalation into these locations. In addition, they are inexpensive and relatively non-toxic materials. Furthermore, many of the electrolytes utilised during cycling, such as aqueous K_2SO_4 and Na_2SO_4 are also benign. The various structural forms of manganese oxides are constructed from different arrangements of one simple unit; namely, the $[MnO_6]$ octahedral unit. These can be connected by sharing oxygens on the corner, edge or face of the octahedra. There are three common structural types into which manganese oxides can be placed; i.e., tunnel structures, layer structures and spinel structures. Tunnel structures

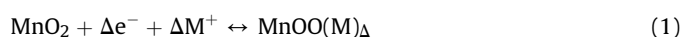
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involve the arrangement of [MnO₆] octahedra in such a manner as to generate tunnels that run in the c-direction through the structure, with width and height equal to between one and three octahedral units [2]. Cations and water can reside in these tunnels depending on their size. Layer structures involve the arrangement of [MnO₆] octahedra such that they form a continuous flat plane. These flat planes are separated by charged species, with the number of these being dependent on the average manganese oxidation state. Water that is hydrogen bonded to the oxygens in the [MnO₆] octahedra can also occupy the interlayer space [2]. Finally, 3D spinel structures of MnO₂ exist in both a fully oxidised form (λ -MnO₂), all the way through to a reduced form, i.e. LiMn₂O₄ [2].

Pseudocapacitive energy storage in these manganese oxides occurs by the reduction of Mn(IV) to Mn(III) via the insertion of an electron from the external circuit, along with the intercalation of a proton or other charged species to maintain charge neutrality [3,4]; i.e.,



The location of these intercalated ions differs between the structural forms of manganese dioxide. In the tunnel structured manganese oxides, cations are drawn into the tunnels if they of compatible size. In the layer structures, cations reside in the space between the layers. In the 3D type structures cations occupy vacant tetrahedral sites. Each of these different structures has varying mass transport properties for proton and cation diffusion [5].

Pyrolusite is a tunnel-structured manganese dioxide with small tunnels that are 1 × 1 octahedral units in size. The tunnels in pyrolusite are formed by long chains of edge sharing [MnO₆] units, joined together by corner sharing [6]. These small tunnels do not provide much room for ions to intercalate, and subsequently the energy barrier for cation hopping is relatively high [7].

Ramsdellite is another tunnel-structured manganese oxide, with tunnels 1 × 2 units in size. The tunnels are formed by two types of long chains of [MnO₆] units formed by edge sharing, one that is one octahedra wide and one that is two octahedra wide, which are then joined together by corner sharing [8]. Ramsdellite, during reduction and cation/proton intercalation forms an intermediate material known as “groutellite”, MnOOM_{0.5} followed by groutite, MnOOM [9].

λ -MnO₂ consists of a cubic close packed arrangement of oxygens, with four tetrahedral and eight octahedral sites per unit cell. The Mn(IV) cations take up half of the octahedral vacancies, with those remaining serving as possible intercalation sites. This 3D spinel structure allows for excellent Li⁺ ion diffusion through the crystal, and thus excellent ionic conductivity [10].

In this work the structural and chemical changes that take place during the electrochemical cycling of ramsdellite, pyrolusite and λ -MnO₂ in an aqueous K₂SO₄ electrolyte have been examined. Understanding the structural changes associated with oxidation and reduction in different phases is necessary for understanding their capacitive variability with potential. An investigation into structural changes will be conducted utilising in-situ X-ray powder diffraction (XRPD) on the manganese oxides of interest while they are undergoing a full cycle of step potential electrochemical spectroscopy (SPECS), an analytical technique where the potential is stepped and then held. At each potential step there is an initial spike in current, followed by a decay. This spike and decay can be modelled to extract capacitive information [11]. The data obtained on how the material crystallographic dimensions change during cycling will be compared with the current passed due to the pseudocapacitive processes obtained from an ex-situ SPECS experiment. These will be extracted from modelling the SPECS decay current for double layer processes and pseudocapacitive

processes. In addition, the variance in double layer capacitance with respect to material state of charge will be investigated.

2. Experimental

2.1. Materials

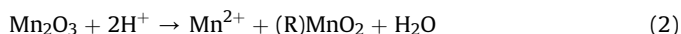
The materials used in this work were γ -MnO₂ (EMD; Delta EMD Australia) KOH (reagent grade (>90%); Sigma-Aldrich), LiOH (reagent grade (>98%); Sigma-Aldrich), K₂SO₄ (Reagent Plus (>99%); Sigma-Aldrich), N-methyl-2-pyrrolidone (Anhydrous; Scharlau) and carbon black (CABOT; LITX200). All solutions prepared were made using Milli-Q ultra-pure water (>18 M Ω ·cm resistivity).

2.2. Pyrolusite synthesis

The pyrolusite used in these experiments was synthesised by heat treatment of γ -MnO₂. This was conducted in air at 350 °C for 24 h in an alumina crucible [12].

2.3. Ramsdellite synthesis

The ramsdellite used in these experiments was prepared from a Mn₂O₃ precursor. The precursor was synthesised by heat treating γ -MnO₂ at 550 °C in air for 24 h in an alumina crucible. This Mn₂O₃ was then allowed to sit in a solution of 0.1 M H₂SO₄ to form ramsdellite by a disproportionation reaction [13], i.e.,



When the reaction was complete, the product was filtered, washed thoroughly with Milli-Q water, followed by drying in air at 60 °C.

2.4. λ -MnO₂ synthesis

The synthesis of λ -MnO₂ first involves the synthesis of LiMn₂O₄, from which the Li ions are subsequently removed. The synthesis of LiMn₂O₄ involved the preparation of a homogenous stoichiometric mixture of LiOH and Mn₂O₃ (synthesised as per section 2.3 above) by ball-milling. This was followed by heating the mixture at 800 °C for 48 h in air. The product was allowed to remain in the furnace as it cooled, after which it was re-milled, and subsequently heated in air at 800 °C for a further 24 h, again remaining in the furnace as it cooled [10].

2.5. Electrochemical cell and electrochemical protocols

2.5.1. Electrochemical cell

The in-situ synchrotron XRPD cell was an in-house made Perspex chamber filled with 0.5 M K₂SO₄, into which both the counter (carbon rod) and reference electrodes (saturated calomel electrode; SCE) were placed. Directly attached to this flooded chamber is a thin section of the cell in which the working electrode was located. This thin section contains Kapton covered windows to allow for X-ray transparency, and the beam length through the solution is ~10 mm. The cell was housed in a spill tray. This chamber was inserted into a baseplate which was anchored to the benchtop. A diagram of the cell can be seen in Fig. 1.

The working electrode in the in-situ cell consisted of AISI-316 (Fe/Cr18/Ni10/Mo3) stainless steel mesh (wire diameter: 0.066 mm; nominal aperture: 0.103 mm, open area: 37%; Good-fellow) dip-coated in a mixture of 80:15:5 (w/w) MnO₂ (<5 μ m particle size, obtained by ball milling followed by sieving), carbon black and polyvinylidene difluoride (PVDF) respectively, which was

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