

Oxidation treatment of γ -MnO₂ and neutron scattering studies

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Manganese oxides show a wide structural variety such as α, β, γ types and are of technological interest as insertion electrodes for secondary lithium batteries. The γ -MnO₂ is used for cathodes of primary 3 V lithium batteries and shows a capacity of about 160 mA h/g.

To improve discharge-charge capacity of γ -MnO₂, chemical treatment with oxidation agent was carried out in order to remove structural protons. It is well known that during the preparation of HTMD at around 250°C the structure changes which is described by the increase of Pr, rutile concentration or De Wolff defects and decrease of Mt, microtwinning, see [1-3]. The point to use an oxidative treatment is to remove the proton without altering the structure. After oxidation, all further manipulations of the manganese oxide were done under an argon inert atmosphere except of the heat treatment from ambient temperature to 300°C.

Nitronium tetrafluoroborate was used as oxidative agent by mixing with the raw material in dehydrated acetonitrile for 24 hours under an Argon flux. The raw material was furnished by Mitsui Kinzoku (EMD, product name TAD3).

The working electrode composed by γ -MnO₂, carbon black and binder with the gravimetric ratio 80:16:4, was packed in stainless cell with polypropylene separator film and lithium metal as anode. The cell contained 1 M LiPF₆/EC+DEC (3:7). To improve contact between electrode and cell, a copper mesh is situated between Li anode and stainless cell, and the cathode is maintained between two aluminium meshes

The cell provides a first discharge-charge capacity up to ca. 248 mA h/g over a voltage range from 2 to 4.2 V vs. Li at a current density of 0.1 mA/cm² (figure 1). By looking at the performance over the first cycles, the fading of the capacity showed a similar behavior between the samples, with the oxidized sample always showing highest discharge capacity at each cycle.

The X-ray spectrum of γ -MnO₂ confirms that no significant structural changes of the structure or appearance of new phases occur as seen in figure 2, by comparison with any heat treatment at temperature higher than 150°C. By analyzing the spectrum, the only effect here is a slight reduction of the size of the tunnels.

To understand the enhancement over oxidation, one must first understand where the different species can be inserted inside the γ -MnO₂. It is already known that two kinds of protons co-exist, called Ruetschi and Coleman [4], but few structural studies were done.

For sample containing protons, neutron scattering experiments are suitable due to the high scattering length of hydrogen. By following structural changes at different temperatures, we cannot assert that the reduction of the peak at about 2 Å is partially due to a de-intercalation of a

proton situated inside an oxygen octahedron as showed by Fillaux and al. [5], see figure 3. But with our oxidative treatment, we can re-intercalate deuterium and by neutron scattering experiment using H/D isotopic substitution extract the specific information about the position of proton and confirm the presence of both type of hydrogen.

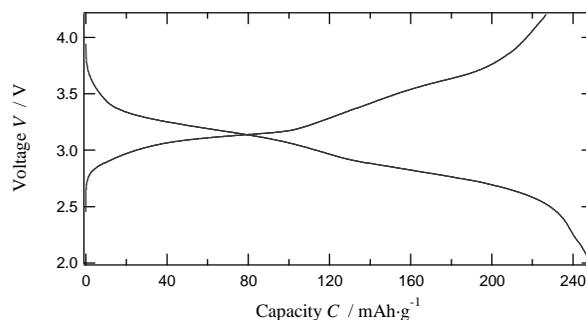


Fig. 1: First cycle profile for γ -MnO₂ oxidized by NO₂BF₄

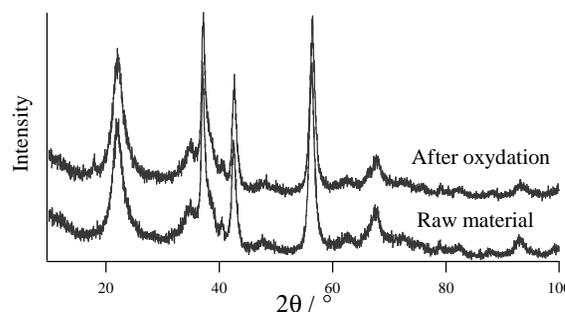


Fig. 2: XRD patterns of γ -MnO₂, raw material, and after an oxidative treatment by NO₂BF₄

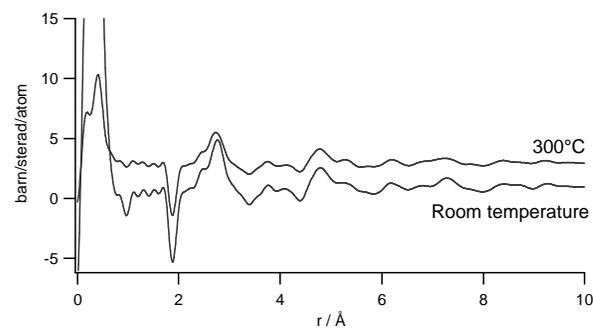


Fig. 3: Neutron scattering of γ -MnO₂ at room temperature and 300°C

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