

α -MnO₂ Nanowires: A Catalyst for the O₂ Electrode in Rechargeable Lithium Batteries**

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Charge storage in rechargeable lithium batteries is limited by the positive electrode, usually the lithium intercalation compound LiCoO₂, which can store 130 mA h g^{−1}.^[1–3] Intense efforts are underway worldwide to discover new lithium intercalation compounds for use as positive electrodes which, it is hoped, may deliver specific capacities of about 300 mA h g^{−1}. However, increasing the capacity significantly beyond this limit is a major challenge requiring a more radical approach, such as replacement of the intercalation electrode by an O₂ electrode, in which Li⁺ from the electrolyte and e[−] from the external circuit combine reversibly with O₂ from the air within a porous matrix containing a catalyst.^[4–8] Although it provides higher capacities than intercalation electrodes, much fundamental work is required to understand and optimize the performance of the O₂ electrode for lithium batteries before it can be considered further for technological application. The nature of the catalyst plays a key role. It is important to identify good catalysts for the electrode reaction before focusing on other tasks, such as reducing the catalyst loading and optimizing porosity, binder, and electrolyte. Herein we show that α -MnO₂ nanowires give the highest charge storage capacity yet reported for such an electrode, reaching 3000 mA h per gram of carbon, or 505 mA h g^{−1} if normalized by the total electrode mass. Furthermore, by avoiding deep discharge, excellent capacity retention has been demonstrated. Finally, the capacities delivered by an O₂ electrode and a conventional intercalation compound are compared.

The reversible oxygen electrode is shown schematically in Figure 1. On discharge, the Li⁺ ions (electrolyte) and e[−] (external circuit) combine with O₂ (air) to form Li₂O₂ within the pores of the porous carbon electrode.^[4–8] Previously, we demonstrated that rechargeability of the Li/O₂ cell involves decomposition of Li₂O₂ back to Li and O₂.^[8] Our earlier studies on the rechargeable Li/O₂ cell focused on electrolytic manganese dioxide (EMD) as catalyst in the oxygen electrode.^[8] Recently, we examined a number of other potential catalyst materials including Co₃O₄, Fe₂O₃, CuO, and CoFe₂O₄.^[9] Such investigations served to demonstrate that the nature of the catalyst is a key factor controlling the

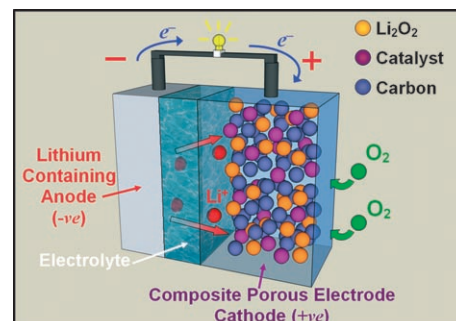


Figure 1. Schematic representation of a rechargeable Li/O₂ battery.

performance of the oxygen electrode, especially the capacity, which is the primary reason for interest in the O₂ electrode. Herein we report on the high capacities that an α -MnO₂ nanowire catalyst can deliver. We also compare the performance of α -MnO₂ with other manganese oxide compounds. Note that the specific capacities are normalized with respect to the mass of carbon in the electrode, as is usual for porous electrodes; this point is discussed at the end of the paper.

Synthesis and characterization of the various MnO_x catalysts and their incorporation into lithium cells with porous electrodes is described in the *Experimental Section*. Powder X-ray diffraction data were collected for all catalysts (see the Supporting Information) and confirmed their identities (α -MnO₂ in bulk and nanowire form, β -MnO₂ in bulk and nanowire form, γ -MnO₂, λ -MnO₂, Mn₂O₃, and Mn₃O₄).

The variation of capacity with cycle number for a porous electrode containing α -MnO₂ nanowires as catalyst is presented in Figure 2a, from which the superior behavior of the α -MnO₂ catalyst is evident. The initial discharge capacity is 3000 mA h g^{−1}, it then drops slightly, rises again to 3100 mA h g^{−1} on cycle 4, before declining steadily thereafter. This may be contrasted with previous reports for EMD, the capacity of which falls below 1000 mA h g^{−1} after one cycle (Figure 2a).^[8] The variation of potential with state of charge for several cycles of α -MnO₂ is shown in Figure 2b. As observed previously for all other catalysts, the discharge voltage is around 2.6 V versus Li⁺/Li⁰.^[8,9] Previous results have demonstrated that the charging potential varies according to the catalyst type.^[9] Values ranging from 4 to 4.7 V versus Li⁺/Li⁰ have been observed, and α -MnO₂ exhibits a charging potential at the lower end of this spectrum, at around 4.0 V. This is another advantage of the α -MnO₂ nanowires, since it is important to minimize the charging potential. Note that α -MnO₂, and many of the other MnO_x compounds described herein, support some Li intercalation. However,

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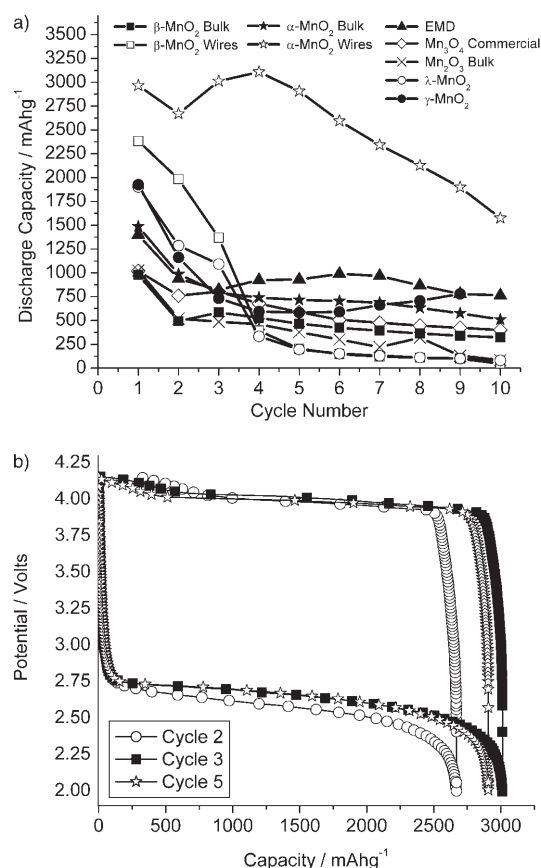


Figure 2. a) Variation of discharge capacity with cycle number for several porous electrodes containing manganese oxides as catalysts: α -MnO₂ in bulk and nanowire form, β -MnO₂ in bulk and nanowire form, γ -MnO₂, λ -MnO₂, Mn₂O₃, and Mn₃O₄. EMD is included herein for comparison but was reported previously.^[8] Cycling was carried out at a rate of 70 mA g⁻¹ in 1 atm of O₂. Capacities are per gram of carbon in the electrode. Lower cutoff potential 2 V. b) Variation of potential with state of charge for the porous electrode containing α -MnO₂ nanowires reported in Figure 2a, cycled at a rate of 70 mA g⁻¹ between 2 and 4.15 V.

such intercalation could not explain the high capacities shown in Figure 2.

A cell containing α -MnO₂ as catalyst was disassembled at the end of discharge, and the electrode investigated by Raman spectroscopy. The results (see the Supporting Information) confirmed that the dominant product of discharge was Li₂O₂, as observed previously for EMD.^[8] Formation and decomposition of Li₂O₂ on discharge and charge were followed by examining the electrode by scanning electron microscopy in different states of charge and discharge (see Figure S3 in the Supporting Information).

The performance of the α -MnO₂ nanowires is compared with that of electrodes containing other manganese oxide catalysts in Figure 2a. The electrodes were constructed in an identical fashion to those containing the α -MnO₂ nanowires and with the same proportion of carbon, catalyst, and binder. The other MnO₂ polymorphs, β , γ and λ , either exhibit lower capacities or capacities that fade very rapidly on cycling; their overall performance is markedly inferior to that of α -MnO₂ nanowires. The performances of Mn₂O₃ and the spinel Mn₃O₄

are also inferior to that of α -MnO₂ nanowires. This is also the case for non-manganese catalysts studied previously.^[9]

Given the catalytic role of the manganese oxides, it is interesting to examine the effect of changing the surface area on the performance. An indication of this can be obtained by comparing the performance of α - and β -MnO₂ catalysts prepared in bulk and nanowire form (Figure 2a). The morphologies are shown in Figure 3. The α -MnO₂ nanowires

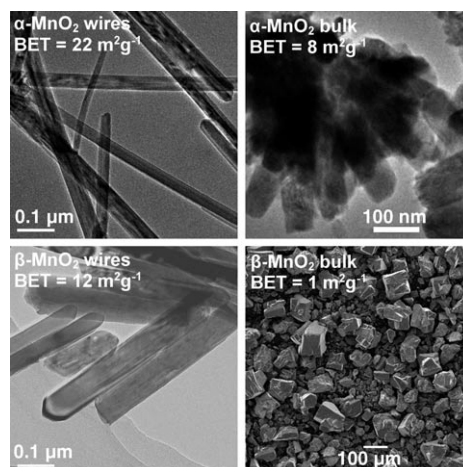


Figure 3. TEM/SEM images of bulk and nanowire forms of α - and β -MnO₂ polymorphs showing their morphologies and surface areas.

are typically 30–40 nm in diameter and can be up to several 100 nm long. The corresponding bulk material also has an elongated morphology, although the aspect ratio is not as high as that of the nanowires, and typical dimensions are around 60–80 nm in diameter and 200–400 nm in length. From Figure 2a it is evident that the nanowires have much higher capacity than the bulk material. This improvement is also observed when comparing nanowire and bulk β -MnO₂ (Figure 3). Here the elongated nature of the structure is not preserved in the bulk material, and this suggests that the enhanced performance of the nanomaterials is due largely to their higher surface area rather than their morphology. However, it is also important to note that the surface area of the α - and β -MnO₂ nanowires differs by less than a factor of two, yet the overall performance of the former on cycling is far superior to that of the latter, that is, the nature of the catalyst is the key, not just the surface area.

Although capacities in excess of 3000 mA h g⁻¹ can be obtained by using α -MnO₂ nanowires as catalyst, not only in the first cycle, it is evident from Figure 2 that the capacities of this and all other catalysts fade. Indeed capacity fading has been a feature of all previous results on such O₂ electrodes.^[4,5,8,9] This suggests that the origin of capacity fading does not lie with the type of catalyst. Voltage polarization occurs at the end of discharge (Figure 2b). If deep discharge is avoided by limiting the discharge capacity to values that avoid such polarization, excellent capacity retention can be obtained, as illustrated in Figure 4. We do not propose limiting the capacity as a technological solution to the problem of capacity fade, but rather as an indicator of the possible origin of fading.

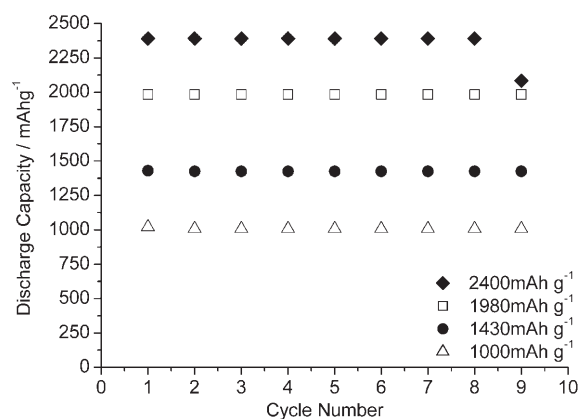


Figure 4. Variation of discharge capacity with cycle number for porous electrodes containing α -MnO₂ nanowires as catalyst when the state of discharge is limited to different degrees. Cycling rate of 70 mA g⁻¹. Capacities per gram of carbon in the electrode.

Even at 2400 mA h g⁻¹ there is some evidence of fade at the end of cycling. The key point is that avoiding polarization (deep discharge) leads to better cyclability. This may reflect the fact that the formation of a large amount of Li₂O₂ in the pores at deep discharge results in their becoming blocked or causes expansion of the electrode leading to loss of contact between electrode particles during subsequent recharge. Such processes are not related to the nature of the catalyst per se and are therefore beyond the scope of this paper. However, work is ongoing to understand and hence minimize capacity fading (e.g., by controlling the electrode pore size/distribution). By better engineering the electrode it should be possible to increase the utilization and thus provide access to the capacities of about 3000 mA h g⁻¹ that are already available for a few cycles.

Why does α -MnO₂ perform better than other closely related manganese oxides? The crystal structure of the α polymorph is that of hollandite and consists of 2 × 2 tunnels formed by edge- and corner-sharing MnO₆ octahedra.^[10] Li₂O can be incorporated within the tunnels, with the O²⁻ ions located at the tunnel centers and the Li⁺ ions coordinated between these central O²⁻ ions and those forming the walls of the tunnels. The ability to accommodate both Li⁺ and O²⁻ within the tunnels suggests the possibility of incorporating Li⁺ and O₂²⁻. Such incorporation is not possible in the other MnO₂ polymorphs or indeed the other MnO_x materials. Since the major role of the catalyst is to promote the reversibility of Li₂O₂ formation, it is tempting to relate these two features and suggest that the ability of the crystal structure to incorporate Li⁺ and O²⁻, most likely near the surface of the material, is pertinent to the good performance of this catalyst. However, identifying Li₂O₂ in the near-surface regions of α -MnO₂ will be a considerable challenge.

Porous gas electrodes are not new; they are ubiquitous in fuel cells, and aqueous batteries containing air cathodes, for example, Zn/air and Fe/air, have been known for sometime. In reporting the behavior of air electrodes, the convention of normalizing the capacity with respect to the mass of carbon has been used for some years, a convention that has been adhered to herein. Reasons for the convention are that carbon

is the dominant component of the porous electrode and the electrode mass increases as discharge proceeds, due to accumulation of Li₂O₂ in the electrode. However, the simplicity of this convention somewhat obscures a direct comparison of the specific capacity of an O₂ electrode with that of an intercalation cathode. The total mass of the cathode at the end of discharge (carbon + binder + catalyst + Li₂O₂) can be used to calculate the specific capacity. However, ultimately it is the contribution to the capacity of the whole battery that matters, and including Li₂O₂ overestimates the mass gained during discharge, since only the mass of O₂ is added to the cell; the Li, which comes from the anode, would be counted twice (The mass of Li is not included in calculating the specific capacity of V₂O₅, for example). Even allowing for this correction, the use of total cathode mass plus O₂ gained is only strictly relevant at the deepest discharge.

Figure 5 shows the specific capacity for the α -MnO₂ nanowires based on total electrode mass at the beginning and end of discharge. Converting the capacity of

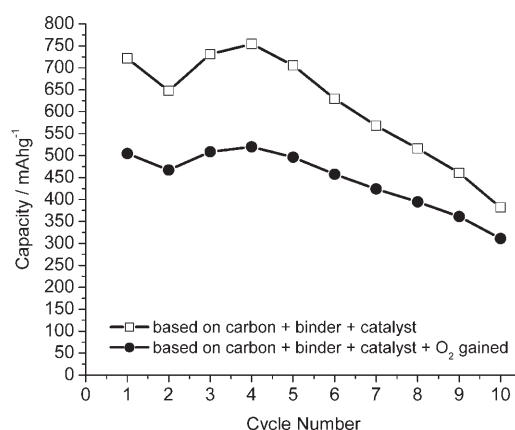


Figure 5. Variation of discharge capacity with cycle number for porous electrodes containing α -MnO₂ nanowires as catalyst, based on total electrode mass at the beginning (carbon + binder + catalyst) and end (carbon + binder + catalyst + O₂) of discharge.

3000 mA h g⁻¹ (carbon) into the specific capacities based on the total masses gives 730 mA h g⁻¹ (carbon + binder + catalyst) and 505 mA h g⁻¹ (carbon + binder + catalyst + O₂). For the restricted capacity cycling shown in Figure 4, the specific capacity of 2400 mA h g⁻¹ (carbon) would correspond to 540 mA h g⁻¹ (carbon + binder + catalyst) and 408 mA h g⁻¹ (carbon + binder + catalyst + O₂). Since in the case of intercalation electrodes only the mass of active material is usually employed to calculate specific capacities, comparison requires addition of the mass of carbon and binder to normalize the charge passed. For a typical mass ratio in a composite cathode containing an intercalation compound of 85:10:5 (active material:carbon:binder), the specific capacities for LiCoO₂, LiCo_{1/3}Mn_{1/3}Ni_{1/3}O₂, LiMn₂O₄ and LiFePO₄, based on the total mass, would be 111, 170, 102, and 132 mA h g⁻¹, respectively. Clearly, the capacities of the O₂ cathode far exceed these values.

The focus of the present paper is the performance of the different manganese oxides as catalysts in the O₂ electrode. To

facilitate comparison between the different catalysts the proportions of carbon:catalyst:binder were fixed. However, if the dimensions of the α -MnO₂ nanowires were reduced to a diameter and length of 10 and 200 nm, respectively, the loading (mass of catalyst in the electrode) could be reduced by 72 % while maintaining the same surface area, and specific capacities of 1076 (carbon + binder + catalyst) and 655 mA h g⁻¹ (carbon + binder + catalyst + O₂) would result.

An estimate of the maximum capacity that can be expected from an O₂ electrode can be made. If we assume a carbon cathode with a porosity of 75 % (such porosity should still ensure electron percolation through the carbon matrix) and use Li₂O₂ formation as the basis but consider the mass gain to be only O₂, a value of 1220 mA h g⁻¹ is obtained. This of course does not allow for the mass of binder or catalyst, and therefore in practice values will be lower. However, it emphasizes that, having identified an optimum catalyst, the next stage must be to minimize the proportions of catalyst and binder.

In summary, the data presented herein show that the use of α -MnO₂ nanowires as catalyst in an oxygen cathode for rechargeable lithium batteries can deliver capacities of 3000 mA h g⁻¹ of carbon or 730 and 505 mA h g⁻¹ based on total electrode masses excluding and including O₂, respectively. These values significantly exceed those of conventional cathodes for rechargeable lithium batteries. By restricting the depth of discharge, it is possible to obtain good capacity retention on cycling, that is, cyclability is not limited by the catalyst but more likely by the porosity of the electrode. Identifying a good catalyst is the necessary first step in optimizing the performance. Having done so, future work will be directed to reducing the loading of catalyst and thus minimizing the total mass of the electrode. Such optimized electrode construction is akin to work on fuel cells, which has seen a reduction in particle size and loading of catalyst, although in that case a major driver is the high cost of Pt rather than the mass of the electrode.

The O₂ electrode is not an immediate technological solution for high-capacity rechargeable lithium batteries. Issues such as a membrane to protect the cathode from ingress of CO₂/H₂O, an optimized electrolyte, safety testing, and extended cycling, must be addressed. However, the capacities reported herein, which exceed those of conventional rechargeable intercalation battery cathodes such as LiCoO₂, LiFePO₄, and Li(Co_{1/3}Ni_{1/3}Mn_{1/3})O₂, encourage further investigation of the O₂ electrode.

Experimental Section

Synthesis and characterization of various MnO_x catalysts: Bulk Mn₂O₃ and Mn₃O₄ were obtained from Aldrich, and bulk β -MnO₂ from Strem. All other MnO₂ catalysts—bulk and nanowire α -MnO₂, nanowire β -MnO₂, bulk γ -MnO₂, and bulk λ -MnO₂—were prepared according to literature procedures.^[11–15]

Powder X-ray diffraction data were collected for all the catalysts on a STOE STADI/P diffractometer operating with FeK α radiation (λ = 1.936 Å). Surface areas were determined by N₂ adsorption/desorption (Micrometrics ASAP2020), and morphologies were examined by SEM (JEOL JSM-5600 and FEI quanta 200F) and TEM (JEOL 2010).

Electrochemical measurements: Electrochemical cycling was carried out in Swagelok TM cells composed of an Li metal anode, electrolyte (1M LiPF₆ in propylene carbonate (Merck)) impregnated into a glass fiber separator and a porous (13 mm diameter) cathode formed by casting a mixture of Super P carbon (MMM), the appropriate catalyst, and Kynar2801 (a copolymer based on poly(vinylidene fluoride)) in molar ratio 95:2.5:2.5. Cathode construction followed our previously published procedure for porous electrodes.^[8] The cells were sealed except for the Al grid window that exposed the porous cathode to the 1 atm of O₂ pressure. The Swagelok cells were located within a chamber filled with 1 atm of O₂, which was itself thermostated at 30 °C. The electrochemical measurements were carried out with a Biologic MacPile cycler.

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