α-MnO₂ Nanowire Catalysts with Ultra-High Capacity and Extremely Low Overpotential in Lithium-Air Batteries through Tailored Surface Arrangement

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\(\alpha\)-Mn\(_2\)O\(_3\) nanowire catalysts with ultra-high capacity and extremely low overpotential in lithium–air batteries through tailored surface arrangement†

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We here report on very high capacity (11 000 mA h g\(^{-1}\)), superb rate capability (4500 mA h g\(^{-1}\) at 5000 mA h g\(^{-1}\)) and high reversibility of Li–air batteries using \(\alpha\)-Mn\(_2\)O\(_3\) NW catalysts mainly associated with their relatively large amount of Mn\(^{3+}\) exposed on the NW surface and a unique mechanism for deposition of discharge products. Our findings of the unprecedentedly fast Li ion transport and reversible formation–decomposition of discharge products attributed to the modified surface arrangement of \(\alpha\)-Mn\(_2\)O\(_3\) NWs suggest a strategy for achieving high-power Li–air batteries in combination with nano-architecture tailoring.

Introduction

Rechargeable lithium batteries have the potential to provide an energy storage solution to depletion of fossil fuel resources and global warming because they are also considered as clean power sources from renewable energy sources for next-generation electric applications such as electric vehicles (EV), portable electric appliances, and large-scale energy storage systems. The energy density of the conventional lithium ion battery cannot meet the stringent requirements of these applications, whereas lithium–air batteries have a significantly high theoretical specific energy of up to 11 140 W h kg\(^{-1}\) because they are based on discharge reaction between Li and oxygen to yield Li\(_2\)O\(_2\). However, regardless of their high energy density, low cycling capability remained as an important hurdle for commercialization. This drawback is mainly accelerated by side reactions leading to lack of electrolytes and formation of unexpected products. The first step of ORR (oxygen reduction reaction) in lithium–air batteries including nonaqueous electrolytes is mainly attributed to the formation of lithium superoxide radicals. Ideally, LiO\(_2\) should further react to form Li\(_2\)O\(_2\) by either disproportionation (2LiO\(_2\) \(\rightarrow\) Li\(_2\)O\(_2\) + O\(_2\)) or electrochemical reduction (LiO\(_2\) + Li\(^+\) + e\(^-\) \(\rightarrow\) Li\(_2\)O\(_2\)). However, the discharge product from ORR was not pure Li\(_2\)O\(_2\) in many conventional electrolyte systems, probably owing to high nucleophilicity of the O\(_2^-\) radical. This superoxide ion (O\(_2^-\)) can easily react with the open-structured electrolyte, which has a low steric hindrance in a highly oxidizing environment. Such high reactivity with the electrolyte tends to cause the formation of organic lithium salts leading to a drastic cyclic degradation. As expected, to overcome this electrochemical side reaction problem, most of the studies have been focused on tailoring and searching out proper electrolytes having significant endurance against nucleophilic attack by O\(_2^-\). Another major issue about lithium–air batteries is their low round trip efficiency arising from very large potential difference between ORR and OER (oxygen evolution reaction). Various types of materials have been adopted for the catalysts to reduce the potential hysteresis and thus to attain high round-trip efficiency. In particular, \(\alpha\)-Mn\(_2\)O\(_3\) has received great attention as an oxide catalyst for lithium–air batteries since its superior catalytic activity was introduced by P. G. Bruce et al. It is worthwhile to note that \(\alpha\)-Mn\(_2\)O\(_3\) atomic structure (octahedral MnO\(_6\)) is similar to that of SmMn\(_2\)O\(_5\) mullite which has been proven to have 45% higher catalytic performance than Pt for NO oxidation reaction, and it is reasonable to expect high catalytic activity of \(\alpha\)-Mn\(_2\)O\(_3\) surfaces. Following Bruce et al., Guan's group demonstrated that MnO\(_2\) directly coated on carbon nanotubes (CNTs) showed superior performance than the one mechanically mixed with CNTs. Giordani et al. proved that MnO\(_2\) showed the best
performance among a wide range of transition metal oxides in terms of Li$_2$O$_2$ decomposition.\textsuperscript{7} Even if manganese oxides with various structures and morphologies, such as MnO$_2$ nano-catalysts,\textsuperscript{8} MnO$_2$ nanowires,\textsuperscript{4} MnO$_2$ hollow spheres,\textsuperscript{9} MnO$_2$ nanorods,\textsuperscript{10} MnO$_2$ with card-house-like structure,\textsuperscript{11} have been synthesized and used as cathode catalysts for Li–air batteries, all of these studies have focused only on the electrochemical performance itself.\textsuperscript{12} Because the relatively good catalytic activity of $\alpha$-MnO$_2$ among various metal oxides was believed to arise from easy accommodation of Li$_2$O$_2$ inside its large 2 $\times$ 2 tunnel structure, many researchers have tried to vary the macrophysical properties such as porosity, the surface-to-volume ratio and so on to enhance the electrochemical properties of lithium–air batteries using $\alpha$-MnO$_2$.\textsuperscript{13} However, this kind of empirical piecemeal approaches without a detailed understanding of the fundamental physical properties governing the catalytic activity of materials has failed to make a breakthrough in the development of commercially available catalysts. Some theoretical studies have shown that a control of exposed surface structure can bring about a couple of remarkable changes in the catalyst properties. Among them, the d-band center model suggested by Nørskov et al. has clearly shown the correlation between the d band center position of catalysts on the exposed surface and their ORR.\textsuperscript{14} Recently, they reported that the Mn ion oxidation state in manganese oxides (MnO$_x$) significantly influenced the catalytic activity for oxygen reduction and oxidation catalysis by using a combination of computational modeling and behavioral experiments. Therein, $\alpha$-Mn$_2$O$_3$ is an excellent bi-functional catalyst for the ORR and the OER.\textsuperscript{15}

Based on the insight gained from the research, we investigated the correlation between the catalytic activity of $\alpha$-MnO$_2$ nanowires and their surface oxidation state of Mn ions. Hence, we here report on $\alpha$-MnO$_2$ nanowires which have relatively reduced Mn ion-terminated surfaces and demonstrate how the surface oxidation state of the Mn ion influences on the reaction kinetics and the discharge product deposition mechanism. Such lower oxidation state surfaces enable more homogeneous nucleation of Li$_2$O$_2$ without toroidal growth and more effective Li$_2$O$_2$ accommodation compared to the $\alpha$-MnO$_2$ nanotubes which have relatively high oxidation states of Mn ion surfaces. As a result, we have successfully proved that the catalytic activity strongly correlated with the surface oxidation states in the $\alpha$-MnO$_2$ catalyst was crucial to exhibit enhanced catalytic activity.

**Results and discussion**

In order to find the properly tuned surface oxidation states in $\alpha$-MnO$_2$, different types of $\alpha$-MnO$_2$ nanomaterials corresponding to nanoparticles (NPs), nanotubes (NTs) and nanowires (NWs) were synthesized via the sol–gel or the hydrothermal route. The morphologies of various $\alpha$-MnO$_2$ nanomaterials were confirmed by TEM analysis. High resolution transmission electron microscopy (HRTEM) images revealed that $\alpha$-MnO$_2$ nanoparticles have a crystallite size of around 20 nm with a nearly equal fraction of different facets. TEM observations of $\alpha$-MnO$_2$ NWs clearly demonstrate randomly aligned nanowire form with a diameter of about 50 nm and the lengths extending to several tens of micrometers, whereas $\alpha$-MnO$_2$ NTs have a typical tubular structure having well-defined inner holes. (Fig. 1) The crystal structures of all $\alpha$-MnO$_2$ nanomaterials have been confirmed by XRD. As shown in Fig. S1 (ESI†), all reflections of $\alpha$-MnO$_2$ nanomaterials were commonly indexed to body-centered tetragonal structure (JCPDS 44-0141) without exception, which belongs to the space group, $I4/m$. There were no impurity peaks and peak shifts related to lattice change or homogeneous strain suggesting that we can exclude all chemical parameters in the variation of their catalytic effects for lithium–air batteries.

Fig. 2a–f well discriminates the surface of $\alpha$-MnO$_2$ NWs from that of $\alpha$-MnO$_2$ NTs. The enlarged HRTEM images in Fig. 2a and d show that the outer shape of $\alpha$-MnO$_2$ NTs is very similar to that of $\alpha$-MnO$_2$ NWs even if the former has its own inner holes.
The growth direction of $\alpha$-MnO$_2$ NWs and NTs could be confirmed from the selected area electron diffraction (SAED) image on the right (Fig. 2c and f) and the fast Fourier transformation (FFT) filtered image (Fig. S2 in ESI†). From SAED analysis and FFT results, it was demonstrated that both $\alpha$-MnO$_2$ NWs and NTs tend to normally grow along the [002] direction which leads to similar structure at the surface. However, the surface oxidation state difference between $\alpha$-MnO$_2$ NWs and NTs is significant as indicated by X-ray photoelectron spectroscopy (XPS) in Fig. 2g. Apparently, Mn 2p$_{3/2}$ binding energy of $\alpha$-MnO$_2$ NWs is little negatively shifted indicating that the exposed Mn ions are more reduced to Mn$^{3+}$ compared to those of $\alpha$-MnO$_2$ NTs. Through this observation, we can conclude that Mn ions in the surface of $\alpha$-MnO$_2$ NWs are more differently coordinated with oxygen than those on $\alpha$-MnO$_2$ NTs. Recently, as mentioned above, a couple of theoretical or experimental studies on the MnO$_2$ catalyst for fuel cell application has shown that Mn$_2$O$_3$ has better ORR and OER activities than MnO$_2$ indicating that the more the Mn$^{3+}$ ions exist on the surface, the higher the catalytic activity of the MnO$_2$ catalyst is.\textsuperscript{15}

Electrochemical performances of lithium–air batteries containing $\alpha$-MnO$_2$ nanomaterials as cathode catalysts are displayed in Fig. 3a and b. The initial galvanostatic ORR–OER profiles in Fig. 3a demonstrate that ORR–OER activities of $\alpha$-MnO$_2$ nanomaterials apparently depend on their morphological characteristics. From this figure, we found that lithium–air cells including nanoparticles, nanowires and nanotubes as the cathode catalysts all show significantly reduced overpotentials compared to the catalyst-free cathode, which make their ORR potentials close to the thermodynamic equilibrium potential of Li$_2$O$_2$ formation. Fig. 3b shows the discharging potential profiles of three nanomaterials at increasing current density (200, 2000, and 5000 mA h g$^{-1}$). Interestingly, lithium–air cells using $\alpha$-MnO$_2$ NWs show an unprecedentedly ultra-high capacity of up to 11 000 mA h g$^{-1}$ (4500 mA h g$^{-1}$) at a high current density of 5000 mA h g$^{-1}$ as well as very low overpotential between ORR and OER enabling high power and high round-trip efficiency to be attained. In contrast, the other $\alpha$-MnO$_2$ nanomaterials fail to meet all aspects of lithium–air cell performances. Even though the capacity accomplished by $\alpha$-MnO$_2$ NTs is significantly higher than that of $\alpha$-MnO$_2$ NPs, discharge capacities of both NTs and NPs are significantly smaller (~1000 mA h g$^{-1}$) at a high current density of 5000 mA h g$^{-1}$. The electrochemical properties obtained at high current density of 5000 mA h g$^{-1}$ (25 times higher than the initial condition), which have been never reported up to now, highlight the advantages of nanowire catalysts. As shown in Fig. 3b, $\alpha$-MnO$_2$ NWs display superior ORR activities not only in capacity (4500 mA h g$^{-1}$) but also in overpotential (plateau potential $\approx$ 2.3 V) compared to previously reported manganese oxide catalysts.

However, $\alpha$-MnO$_2$ NPs have the largest BET surface area and pore concentration, and those of $\alpha$-MnO$_2$ NWs are almost identical with those of $\alpha$-MnO$_2$ NTs. Therefore, one could not satisfactorily explain the ORR–OER activities of $\alpha$-MnO$_2$ nanomaterials based on their macro-physical parameters like surface area and pore concentration, which have been commonly used as the most general parameters affecting the catalytic activity of catalyst materials. Furthermore, the four-point probe electrical conductivity of the cathodes composed of $\alpha$-MnO$_2$ nanomaterials is also similar irrespective of their morphologies. These observations (Table S2 in ESI†) strongly suggest that other fundamental physical properties should be considered for explaining the superior performance of NWs. A reason for the worst catalytic activity of nanoparticle catalysts may be attributed to their highly packed electrode structure interfering with O$_2$ diffusion and Li$_2$O$_2$ accommodation. Key factors explaining the difference between nanowire and nanotube performances could be clarified by ex situ SEM and TEM observation of the samples after the initial ORR and OER.

Fig. 4 compares the morphology of $\alpha$-MnO$_2$ NWs with that of $\alpha$-MnO$_2$ NTs after the initial ORR. TEM images in Fig. 4a and b clearly exemplify that a very thin layer of Li$_2$O$_2$ is uniformly deposited on $\alpha$-MnO$_2$ NWs, while the surface of $\alpha$-MnO$_2$ NTs has big agglomerates of Li$_2$O$_2$. Furthermore, $\alpha$-MnO$_2$ NWs themselves and the air electrode including $\alpha$-MnO$_2$ NWs tend to be coated with unique lamellar-shaped discharge products having very high surface area after ORR, as shown in Fig. 4c. This phenomenon may be due to the reduced oxidation states of surface Mn ions associated with the reaction kinetics during
ORR enabling homogeneous distribution and unique plate- or lamellar-shaped formation of discharge products. The homogeneous Li$_2$O$_2$ deposition on NW surfaces would nucleate columnar growth of small particles leading to lamellar structure of the air-electrode. Such lamellar morphology would provide high kinetic pathways for Li$_2$O$_2$ formation and decomposition leading to unusually high power performance of the NW catalyst.\(^\text{16}\)

In contrast, the other air electrodes including $\alpha$-MnO$_2$ NTs or $\alpha$-MnO$_2$ NPs, and catalyst-free air electrodes commonly show a typical toroidal growth of Li$_2$O$_2$ from large agglomerates. Such large Li$_2$O$_2$ structure definitely makes the kinetic performance worse and acts as a significant hurdle against its reversible formation and decomposition (Fig. S4 in ESI†).

To avoid the formation of thermodynamically stable and insulating discharge products such as lithia (Li$_2$O) induced by deep discharging (leading to irreversible capacity loss), we conducted galvanostatic discharge–charge cycling experiments with the limited utilization of capacity ($1000 \text{ mAh g}_\text{carbon}^{-1}$). The OER overpotential of $\alpha$-MnO$_2$ NWs under this limited capacity condition is a little higher than that obtained between 2.0 and 4.5 V vs. Li/Li$^+$. We here speculate that the increase of overpotential with the limited capacity may be attributed to strong bonding between Li$_2$O$_2$ and an initial bare surface of...
α-MnO₂ NWs or its deep embedment into the open-structured surface frame with a 2 × 2 channel. However, Fig. 5a indicates that α-MnO₂ NWs still show the lowest overpotential compared to α-MnO₂ NPs and α-MnO₂ NTs. At the 10th cycle, α-MnO₂ NPs and NTs undergo drastically increased polarization followed by a serious cyclic degradation, whereas α-MnO₂ NWs still maintain great round-trip efficiency without the increase of polarization (Fig. 5b). XPS analyses show that the main discharge product of lithium–air batteries using α-MnO₂ NWs and NTs is Li₂O₂. Li 1s and O 1s partial spectra of α-MnO₂ NWs and α-MnO₂ NTs commonly indicate that a peak attributed to Li₂O₂ is formed after ORR. During the 10th OER, α-MnO₂ NW catalysts can facilitate the effective decomposition of Li₂O₂, whereas the catalytic activity of α-MnO₂ NTs is too much deteriorated to decompose Li₂O₂. (Fig. 5c and d) The evolution of C–O or C–O=C bonds besides Li₂O₂ in Fig. 5d demonstrates that there is still an impeditive lithium salt formation through the electrolyte decomposition by O²⁻ ions, which can be further reduced by electrolyte modification.²,¹⁷

Conclusions

In summary, based on the theoretical insight from research on the catalytic effect of manganese oxides due to their oxidation states, 1D α-MnO₂ nanomaterials having a similar macro-physical parameter except surface Mn ion oxidation states have been successfully synthesized under the hydrothermal conditions. The highest reversibility of Li–air cells using these α-MnO₂ NWs was mainly associated with their relatively large amount of Mn³⁺ exposed to the surface. This result suggests that the surface oxidation states can be the dominant factor with an impact on the deposition mechanism of discharge products and ORR/OER catalyst performance of lithium–air batteries.

Acknowledgements

This research was supported by POSCO-RIST research program (2012K110) and by the NRF of Korea through WCU program (Grant No. R-31-10083-0). K. Song acknowledges NRF (National Research Foundation of Korea) Grant funded by the Korean Government (NRF-2013H1A2A1033981-Global PhD Fellowship Program).

Notes and references