Ru/α-MnO$_2$ nanotube catalysts for electrochemical decomposition of Li$_2$O$_2$ in Li-O$_2$ batteries

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ABSTRACT: $\alpha$-MnO$_2$ nanotubes (MNT) decorated with ruthenium nanoparticles (x wt% Ru/MNT) were prepared by a simple reduction and mechanical stirring method, which aims to design a highly active electrocatalyst for the Li-O$_2$ batteries. Ru nanoparticles were dispersed uniformly on the surface of the MNTs. The electrocatalytic activities of as-prepared samples were evaluated by following the Li$_2$O$_2$ decomposition during the charging process. The time-resolved oxygen evolution reaction (OER) kinetics for Li-O$_2$ cells charged galvanostatically and potentiostatically was systematically investigated using operando synchrotron radiation powder X-ray diffraction (SR-PXD). Even a small amount of the Ru decoration on the MNTs largely enhanced the OER efficiency in the Li-O$_2$ batteries. The Li$_2$O$_2$ decomposition for the electrodes with x wt% Ru/MNT catalysts during galvanostatic and potentiostatic charging processes followed pseudo-zero-order kinetics. Furthermore, it was found that the OER kinetics for a cell with the 2 wt% Ru/MNT sample charged at a constant potential of 4.3 V was faster than that for a cell with home-made Ru nanoparticles, which may be attributed to the synergistic effects between the Ru nanoparticles and the MNT support. These results indicated that the x wt% Ru/MNT represented a promising cathode electrocatalyst for promoting the OER kinetics in Li-O$_2$ batteries. In addition, the effect of applied potential on the OER kinetics for the Li-O$_2$ cells with 2 wt% Ru/MNT catalyst was also investigated by SR-PXD.

Keywords: Ru nanoparticle, MnO$_2$ nanotube, Li-O$_2$ battery, galvanostatic and potentiostatic charging, electrocatalyst, operando synchrotron radiation powder X-ray diffraction (SR-PXD).
1. Introduction

Li-O\textsubscript{2} battery has been attracting increasing attention and R&D efforts as a promising power source for the electric vehicles (EVs) due to its far higher theoretical energy density than that of conventional Li-ion battery [1, 2]. In a nonaqueous Li-O\textsubscript{2} system, the ideal electrochemical reaction is \(2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2\), with the battery discharge described by forward direction (oxygen reduction reaction (ORR)) and charge described by the reverse direction (oxygen evolution reaction (OER)) [3]. However, it has been well-known that the real battery electrochemistry is considerably more complicated. So far, substantial challenges obstruct the developments of Li-O\textsubscript{2} batteries, such as the poor stabilities of electrolyte and O\textsubscript{2} electrode, large overpotential, and low energy efficiency [4, 5]. Although the real role of the electrocatalyst in Li-O\textsubscript{2} battery is still under intense debate [1, 6], it has been widely accepted that the ORR is catalytically insensitive, since carbon alone could provide a sufficient catalytic promotion [5, 7], while the employment of electrocatalyst can facilitate the OER kinetics [8, 9]. Thereby, there has been much activity in the electrocatalyst development for the OER as a way to lower the cell overpotential, since the overpotential mainly comes from the OER.

A number of electrocatalysts have been widely investigated in Li-O\textsubscript{2} batteries, including carbonaceous materials [10, 11], transition metal oxides [12, 13], precious and non-precious metals [7, 14, 15]. Although precious metals have shown high stability and superior catalytic activity during the OER [14, 16, 17], its cost and scarcity inevitably limit their practice application in Li-O\textsubscript{2} batteries. In an attempt to develop an electrocatalyst competing with noble metal, noble metal dispersed on supporting materials have been reported [7, 18]. Equally, among transition metal oxides, manganese oxide (MnO\textsubscript{2}) stands out not only as the trade-off between cost and electrocatalytic activity [6], but also as a catalyst support for the Li-O\textsubscript{2} batteries [3, 19, 20]. In our previous work, highly dispersed Pt nanoparticles deposited on \(\alpha\text{-MnO}_2\) nanotubes (Pt/MNT) were developed, which exhibited an excellent electrocatalytic activity during the OER [3]. Ru- or RuO\textsubscript{2}-based electrocatalyst has been recently demonstrated to display a bifunctional electrocatalytic activity (towards both the ORR and OER) for Li-O\textsubscript{2} batteries [7, 21-23]. Moreover, Reier et al., proved by the surface-sensitive cyclic voltammetry study that intrinsic catalytic activity of Ru nanoparticles for the OER is higher than that of Pt nanoparticles [24]. So far, MNT supported by Ru nanoparticles as a cathode electrocatalyst has not been reported.

Until now, most evaluations of electrocatalysts have depended on galvanostatic discharge-charge measurements, with no quantitative evidence of what kind of electrochemical reaction that occurs. Therefore, it is hard to judge whether it is a genuine electrocatalytic effect related to the Li\textsubscript{2}O\textsubscript{2} decomposition during charge. Model electrode assembled from discharged state (i.e., Li\textsubscript{2}O\textsubscript{2}-filled electrode) is a useful tool for investigating the fundamental knowledge of charging process and providing mechanism insights into the OER kinetics [8, 25, 26]. In addition, addressing the key factors for the electrochemical decomposition of Li\textsubscript{2}O\textsubscript{2} is urgently needed. Great efforts have been devoted to exploring the OER kinetics and \textit{ex situ} techniques nearly dominate in those works [27-29]. However, artifacts from post treatments were inevitably introduced into the \textit{ex situ} measurements due to their post-mortem nature. This not only influences the analytic accuracy, but also leads to loss
of the important information. Operando study can provide an efficient, accurate and reliable evaluation in the electrochemical reaction under the battery operation. Moreover, it can give insight into the time-resolved kinetics throughout the whole electrochemical process as well as dynamic factors [30]. In our previous work, by mapping the charge process of the Li-O2 battery galvanostatically using operando synchrotron radiation powder X-ray diffraction (SR-PXD), the catalytic performances of the electrocatalysts were evaluated by following the Li2O2 decomposition [3, 31]. Although probing on the time-resolved OER kinetics for a cell charged potentiostatically is also critically and urgently needed, it has not yet been established.

Herein, MNT decorated by Ru nanoparticles (Ru/MNT) were synthesized via a simple reduction and mechanical stirring method. The electrocatalytic activities of as-prepared samples were evaluated by following the decomposition of Li2O2 during the charging process in the Li-O2 cells. In addition, the time-resolved OER kinetics for the Li-O2 cells charged galvanostatically and potentiostatically was systematically studied using operando SR-PXD. Furthermore, the key factors (e.g., catalyst amount and composition, and applied potential) influencing the OER efficiencies were investigated. To the best of our knowledge, this is the first time to investigate the real-time OER kinetics for Li-O2 batteries under potentiostatic charge conditions by SR-PXD.

2. Experimental

2.1. Preparation of x wt% Ru/MNT (x=0, 0.5 and 2)
All chemicals were of analytical grade and used without any further purification. MNT was synthesized by a hydrothermal treatment, which has been reported in previous work [3, 32]. Briefly, potassium permanganate (VII) (KMnO4, 0.597 g, Merck) was dissolved into deionized water (70 mL). Under vigorous stirring, hydrochloric acid (HCl, 37%, 1 mL, Prolabo) was added dropwise to the solution. After stirring for 30 min, the resultant hydrothermal precursor was then transferred to an autoclave, and maintained at 140 °C for 12 h. After the hydrothermal crystallization, the resultant product, MNT, was filtered and washed with deionized water, and then dried at 60 °C overnight.

The preparation of x wt% Ru/MNT (x=0.5 and 2) was carried out by a simple reduction and mechanical stirring method. An appropriate volume of sodium borohydride (NaBH4, 0.4 M, Merck) was added dropwise into ruthenium (III) chloride hydrate (RuCl3·3H2O, 0.1 wt%, Alfa Aesar) aqueous solution under magnetic stirring for 30 min at 60 °C. As-prepared MNT (0.1 g) was then added to the reaction mixture and kept under stirring for 24 h at the room temperature. The resultant product was filtered and washed with deionized water, and then dried at 60 °C for overnight. X wt% Ru/MNT (x=0.5 and 2) was obtained by adjusting the dosages of NaBH4 and RuCl3·3H2O, according to the theoretical values of raw materials. Pure Ru nanoparticles (home-made Ru nanoparticles) were synthesized under similar conditions, which acted as a reference to compare the catalytic activities with supported samples.

2.2. Preparation of Li2O2-filled electrode, assembly of electrochemical cell, and electrochemical testing
The preparation of Li$_2$O$_2$-filled electrode and assembly of electrochemical cell were performed inside an ultra-high purified argon filled glove box (H$_2$O and O$_2$ < 1 ppm). The electrode construction is similar with that of the positive electrode reported previously [3, 31], which consisted of Super P carbon (lithium battery grade, Erachem Comilog), x wt% Ru/MNT or home-made Ru nanoparticles, Kynar 2801 (a copolymer based on PVDf, Arkema), silicon (Si, 99.5%, Alfa Aesar), and Li$_2$O$_2$ powder (95%, Acros Organics) in a weight ratio of 40:8:7:10:35. The effect of electrocatalyst amount on the Li$_2$O$_2$ decomposition was also studied by adjusting the weight ratio of the components (44:4:7:10:35 or 46:2:7:10:35). Si acted as an inert reference to quantify the residual amount of Li$_2$O$_2$ for the electrode, since it can provide strong and stable diffraction peaks in the XRD patterns. Firstly, Super P carbon, as-prepared catalyst, Si, and Li$_2$O$_2$ were mixed by high energy milling for 1 h. Kynar binder and acetone solvent (≥ 99.0%, Fluka) were then added to the mixture to prepare a slurry, which was further hand-milled for 30 min. The slurry was cast onto an aluminum mesh with a diameter of 13 mm. After the acetone evaporated, the obtained electrodes were further dried in a vacuum oven (Buchi Glass Oven B-585) at 120 °C for 5 h.

The electrochemical cells was assembled in an aluminium pouch cell (i.e., “coffee bag” cell) with the following components: a Li foil negative electrode, a Solupor separator presoaked in electrolyte (1 M LiPF$_6$/propylene carbonate (PC), Ferro, Parolyte), and a Li$_2$O$_2$-filled positive electrode described above.

All electrochemical testing for the charging process were carried out with a potentiostat (SP-240, Bio-Logic SAS). A constant current density of 40 mA·g$^{-1}$Li$_2$O$_2$ was conducted for galvanostatic measurements during charging for 15 h, while potentiostatic measurements were performed at applied potentials of 4.1-4.5 V for 4 or 7.25 h.

2.3. Characterization

The morphology and element analyses of samples were examined by scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS-Zeiss 1550 with Aztec EDS). Transmission electron microscopy (TEM, JEOL JEM-2010F) was used to obtain the detailed size and crystal information of as-prepared catalysts, operating at an accelerating voltage of 200 kV. In situ XRD analysis was carried out to study the electrochemical decomposition of Li$_2$O$_2$, which was performed in a transmission mode using a STOE diffractometer with a position-sensitive detector and Cu Kα1 radiation with the wavelength ($\lambda$) of 1.5406 Å, operating at 45 kV and 40 mA. To further study the time-resolved OER kinetics, operando SR-PXD was conducted using beamline 1711 with $\lambda$ of 0.994 Å at Max IV Laboratory in Lund, Sweden [33]. It has been reported that the electrochemical decomposition of Li$_2$O$_2$ can be accelerated under the continuous X-ray irradiation [2]. In order to avoid the influence of X-ray illumination, the frames were collected every 15 or 30 min by an Oxford diffraction Titan CCD area detector. Lanthanum hexaboride (LaB$_6$, SRM-660) was used as a reference material for calibrating some instrument parameters (e.g., sample-to-detector distance and detector tilt angle). Each frame is an integrated data collected during an exposure time of 20 s, which was later converted a plot of intensity vs. 20 by Fit2D program [34]. FullProf program was used to refine the in situ XRD and operando SR-PXD patterns and analyze weight fractions of Si and Li$_2$O$_2$ ($F_{Si}$ and $F_{Li_2O_2}$) for the Li$_2$O$_2$-filled electrodes [35]. The residual Li$_2$O$_2$ ratios ($R$) for the Li-O$_2$ cell before, during or after the charging process were
calculated from the equation S1 in Supplementary Information (SI).

3. Results and discussion

Figure 1. SEM images of (a) MNT and (b) 2 wt% Ru/MNT, TEM images of (c) MNT and (d) 2 wt% Ru/MNT, and (e) HRTEM image of 2 wt% Ru/MNT.

The SEM images of the MNT and 2 wt% Ru/MNT samples are shown in Figures 1a and 1b. It can be seen that the MNT displayed “tube-like” shape with a length of 1-1.5 μm and a width of 80-100 nm (Figure 1a). Dispersed Ru nanoparticles were attached to the surface of the 2 wt% Ru/MNT sample (Figure 1b). The Ru content (2.4 wt%) obtained from the EDS analysis was in good agreement with the feed ratio (2 wt%) in the synthesis, indicating that the synthesis of the x wt% Ru/MNT samples was successful and controllable. Detailed particle information was obtained by TEM. In Figure 1c, the nanotube shape of the MNT can clearly be observed and the tube inner diameter was about 40-60 nm. For the 2 wt% Ru/MNT sample, the Ru nanoparticles were distributed on the surface of MNTs (Figure 1d), which was in agreement with the SEM image. The Ru particle size in the 2 wt% Ru/MNT sample was about 5-10 nm. In Figure 1e, the HRTEM image of 2 wt% Ru/MNT displays well-defined lattice fringes with distances of 0.485 and 0.242 nm, corresponding to the (200) lattice plane of the tetragonal-structure α-MnO₂ (JCPDS Card No. 04-007-2142) [36], and the (101) lattice plane of the hexagonal-structure Ru (JCPDS Card No. 06-0663) [37], providing a direct evidence of a successful loading of the Ru nanoparticles on the surfaces of MNTs.
Figure 2. (a) The residual Li$_2$O$_2$ ratios for the electrodes with different electrocatalysts (MNT, 0.5 wt% Ru/MNT, 2 wt% Ru/MNT and home-made Ru nanoparticles) after charging for 15 h at a constant current density of 40 mA·g$^{-1}$Li$_2$O$_2$·, (b) the operando SR-PXD patterns of an electrode with 2 wt% Ru/MNT collected every 30 min during charging for 15 h at a constant current density of 40 mA·g$^{-1}$Li$_2$O$_2$·, (c) the curve (−) and linear curve fitting (−·−) of Li$_2$O$_2$ degradation, and (d) the charging profile of the same cell as in (b) and (c) during the operando SR-PXD measurement.

The electrocatalytic performance of as-prepared samples was evaluated by following the Li$_2$O$_2$ decomposition for the Li-O$_2$ cells charged for 15 h at a constant current density of 40 mA·g$^{-1}$Li$_2$O$_2$ using in situ XRD and operando SR-PXD. Figure 2a shows the residual Li$_2$O$_2$ ratios for the electrodes with different catalysts after 15 h of charging. There is a significant difference between the residual Li$_2$O$_2$ ratio for the electrode with the MNT catalyst (89.1 %) and the theoretical value (49.2 %) calculated from the charge capacity, indicating that the OER of a cell with the MNT was accompanied with considerable parasitic reactions. The residual Li$_2$O$_2$ ratio for an electrode with 0.5 wt% Ru/MNT was 66.5 %, indicating that even a small amount of Ru decoration on the MNT enhanced the OER kinetics. In addition, the residual Li$_2$O$_2$ ratio of 51.4 % for an electrode with 2 wt% Ru/MNT sample was close to that of 50.7 % for the electrode with home-made Ru nanoparticles and the theoretical value of 49.2 %, indicating that appropriate Ru decoration on the MNT could suppress the side reactions during the OER. The influence of the catalyst amount on the Li$_2$O$_2$ degradation was also studied by adjusting the catalyst loading. The residual Li$_2$O$_2$ ratios for the electrodes with 2, 4, and 8 wt%
representative catalyst (2 wt% Ru/MNT) after charging for 15 h at a constant current density of 40 mA·g\(^{-1}\)\(\text{Li}_2\text{O}_2\) can be seen in Figure S1 in SI. Since the OER of a Li\(\text{O}_2\) cell with 8 wt% catalyst exhibited the highest OER efficiency, 8 wt% is a standard weight ratio for the catalyst loading in this study, unless otherwise specified. Note although 8 wt% catalyst shows the highest catalytic effect in different amounts of catalyst loading, the turnover frequency of 4 wt% catalyst is 1.8 times than of 8 wt% catalyst.

To further study the real-time OER kinetics of a Li\(\text{O}_2\) cell with 2 wt% Ru/MNT catalyst under galvanostatic charge, *operando* SR-PXD was employed to track the Li\(\text{O}_2\) degradation. Figure 2b displays the *operando* SR-PXD patterns of this electrode collected every 30 min during the charging process at a constant current density of 40 mA·g\(^{-1}\)\(\text{Li}_2\text{O}_2\) (JCPDS File No: 04-013-3506) and Si (JCPDS File No: 04-014-0211) crystalline phases were observed. Note that the significant change in the intensity of Si peaks was attributed to the recovering injection of synchrotron-based X-ray beam. 48.6 % of the Li\(_2\text{O}_2\) was decomposed after 15 h of charging (Figure 1c), which was close to the theoretical value of 50.4 % calculated from the charge capacity. Since the Li\(_2\text{O}_2\) decomposition curve was approximately linear with respect to the charging time, as shown in Figure 1c, *pseudo*-zero-order kinetics can be assumed to quantify the corresponding decomposition rate constant \(k\) from the equation S2 in SI. Based on the curve fitting, it can be concluded that the Li\(_2\text{O}_2\) decomposition in a cell with 2 wt% Ru/MNT followed the zero-order kinetics, and the decomposition rate constant was 3.3528 h\(^{-1}\). Figure 1d shows the charging profile for the same cell under the *operando* SR-PXD measurement. Note that the curve oscillation is caused by periodic temperature fluctuance in the SR-PXD room.
Figure 3. (a) Net current density vs. time (Inset: the enlarged part enclosed by the dashed arrow in (a)), (b) capacity vs. time for the Li-O_2 cells with different catalysts (MNT, 0.5 wt% Ru/MNT, 2 wt% Ru/MNT and home-made Ru nanoparticles) charged at a constant potential of 4.3 V, and the curves (−) of Li_2O_2 decomposition calculated from the charge capacity and the curves (−−) of Li_2O_2 decomposition calculated from the *operando* SR-PXD results in the cells with (c) MNT, (d) 0.5 wt% Ru/MNT, (e) 2 wt% Ru/MNT, and (f) home-made Ru catalysts (Inset: the enlarged part enclosed by the red circle in the corresponding curves).

The OER kinetics for the Li-O_2 cells with different catalysts (MNT, 0.5 wt% Ru/MNT, 2 wt% Ru/MNT and home-made Ru nanoparticles) under potentiostatic charging conditions was also studied *via* following the Li_2O_2 decomposition with *operando* SR-PXD. Considering that the oxidation of Li_2O_2 for a cell charged galvanostatically run above 4.2 V (Figure 2d) and the potential for side reactions in the electrocatalyst-containing Li-O_2 cell was about 4.4 V (see Figure S2 in SI), all the cells were charged at a constant potential of 4.3 V. Figures 3a and b show the potentiostatic charging profiles for the different cells during the *operando* SR-PXD measurements. As presented in Figure 3a, the net oxidation current densities obtained from the
cells with 0.5 wt% Ru/MNT and 2 wt% Ru/MNT samples were much higher than that for a cell with MNT, indicating that as-prepared Ru/MNT electrocatalysts can promote the OER in the cells under potentiostatic charging conditions. The charge capacity \(759 \text{ mAh/g}_{\text{Li}_2\text{O}_2}\) for a cell with 2 wt% Ru/MNT after the charging for 7.25 h was close to that \(787 \text{ mAh/g}_{\text{Li}_2\text{O}_2}\) for a cell with the home-made Ru nanoparticles (Figure 3b), which was in good agreement with the results from galvanostatic charging studies. In addition, the OER kinetics for each cell was studied. As shown in Figures 3c-f, the residual \(\text{Li}_2\text{O}_2\) ratios for the different electrodes calculated from the operando SR-PXD results were very close to those calculated from the charge capacities. This indicates that the \(\text{Li}_2\text{O}_2\) decomposition is the main reaction during charging at 4.3 V. Note that a sluggish decomposition of \(\text{Li}_2\text{O}_2\) was observed in all the cells during the beginning 30 min of charging (i.e., the residual \(\text{Li}_2\text{O}_2\) ratios calculated from the operando SR-PXD results were higher than those calculated from the charge capacities), as presented in the insets of Figures 3c-f, which was also observed in previously published works [2, 38]. This can be hypothesized that different chemical compositions might exist on the surface of \(\text{Li}_2\text{O}_2\) particles, which may be oxidized firstly during the beginning of the charging process, leading to the sluggish oxidation of \(\text{Li}_2\text{O}_2\). For example, Harding et al., demonstrated that the surface of commercial \(\text{Li}_2\text{O}_2\) bulk could be covered by the amorphous LiOH [38]. In addition, it has been reported that \(\text{Li}_2\text{CO}_3\) existed on the \(\text{Li}_2\text{O}_2\) surface could also influence the kinetics of \(\text{Li}_2\text{O}_2\) degradation during the beginning of charging [39].

Pseudo-zero-order kinetics can also be assumed here and the corresponding decomposition rate constant \(k\) was obtained from curve fitting according to equation S2 in SI, as presented in Figure S3 in SI. The \(\text{Li}_2\text{O}_2\) decomposition kinetics in a cell with 2 wt% Ru/MNT \((k_{2 \text{ wt\% Ru/MNT}} = 10.2143 \text{ h}^{-1})\) was 2.5 times faster than that in a cell with MNT \((k_{\text{MNT}} = 2.8384 \text{ h}^{-1})\), confirming that the Ru decoration can enhance the OER kinetics. In addition, the promoting effect by suitable loading of Ru on the MNT was even larger than that by pure home-made Ru nanoparticles \((k_{\text{home-made Ru}} = 9.2899 \text{ h}^{-1})\) under potentiostatic charging conditions, which may be attributed to synergistic effects between the deposited Ru nanoparticles and the MNT support.
Figure 4. (a) The charging profiles of the Li-O\textsubscript{2} cells with 2 wt% Ru/MNT catalyst during charging for 1.5 h at a constant current density of 40 mA·g\textsubscript{Li\textsubscript{2}O\textsubscript{2}}\textsuperscript{−1}, (b) Net current density vs. time, and (c) capacity vs. time for the corresponding cells during charging for the following 6 h (after initial galvanostatic charge of 1.5 h) at constant potentials of 4.1, 4.3 and 4.5 V, and the curves (−) of Li\textsubscript{2}O\textsubscript{2} decomposition calculated from the charge capacity and the curves (−·−) of Li\textsubscript{2}O\textsubscript{2} decomposition calculated from the operando SR-PXD results for the cells charged at constant potentials of (d) 4.1 V, (e) 4.3 V, and (f) 4.5 V.

The effect of applied potential on the OER for a Li-O\textsubscript{2} cell with as-prepared catalyst was also investigated. In order to mitigate the effect of the sluggish kinetics during initial charging process, the cells were charged at a constant current density of 40 mA·g\textsubscript{Li\textsubscript{2}O\textsubscript{2}}\textsuperscript{−1} for 1.5 h. As seen in Figure 4a, the plateaus of the cells charged galvanostatically were around 4.25 V. The net current densities and capacities for the cells charged at different potentials (after initial galvanostatic charge) are shown in Figures 4b and 4c, respectively. It can be seen that the net current densities and capacities obtained from the cells charged at 4.3 and 4.5 V were much higher than those from the cell charged at 4.1 V, indicating that the potential threshold does exist in the OER. The time-resolved OER kinetics for each cell was also studied by operando
SR-PXD, as presented in Figures 4d-f. The residual Li$_2$O$_2$ ratios for the cells charged at constant potentials of 4.1 and 4.3 V (calculated from the SR-PXD results) were very close to the theoretical values (calculated from the charge capacities), as presented in Figures 4d and 4e. However, the difference between the residual Li$_2$O$_2$ ratio calculated from the SR-PXD result and charge capacity was obvious when a constant potential of 4.5 V was applied (Figure 4f), indicating that a number of parasite reactions (e.g., electrolyte decomposition) existed in the cell running at a high charge potential. This was in agreement with our control experimental result (Figure S2 in SI) and the previous finding by Xu et al., who has shown that PC decomposition occurred during the cell charge at a high potential [40]. Pseudo-zero-order kinetics also applied here and the corresponding decomposition rate constant $k$ was obtained (Figure S4 in SI). It was found that the cell charged at 4.3 V exhibited the fastest OER kinetics ($k_{4.3V} = 11.6391$ h$^{-1}$), compared to those for the cells charged at 4.1 V ($k_{4.1V} = 2.4217$ h$^{-1}$) and 4.5 V ($k_{4.5V} = 6.6829$ h$^{-1}$).

4. Conclusions

α-MnO$_2$ nanotubes decorated with Ru nanoparticles were successfully synthesized by a simple reduction and mechanical stirring method. Ru nanoparticles were uniformly dispersed on the surface of the MNTs. The electrocatalytic activities of as-prepared samples were evaluated by following the Li$_2$O$_2$ decomposition during the charging process of the Li-O$_2$ cells. The results presented that a small amount (2 wt%) of Ru decoration on the MNTs and a suitable amount (8 wt%) of catalyst loading in the electrode were enough to promote the OER of Li-O$_2$ cells. The time-resolved OER kinetics for the Li-O$_2$ cells charged galvanostatically and potentiostatically was systematically investigated using operando SR-PXD. It is found that the Li$_2$O$_2$ decomposition in the Ru/MNT-containing electrode during galvanostatic and potentiostatic charging processes followed pseudo-zero-order kinetics. In addition, the OER in a cell with the 2 wt% Ru/MNT charged at a constant potential of 4.3 V run even faster than that in a cell with home-made Ru nanoparticles, which could be attributed to the synergistic effects between the deposited Ru nanoparticles and the MNT support. Furthermore, the cell charged at a constant potential of 4.3 V exhibited a faster OER kinetics than those charged at constant potentials of 4.1 and 4.5 V, indicating that a suitable charge potential is important to meet kinetic requirement of the OER (i.e., activity issue) and restrain side reactions (i.e., selectivity issue).

Acknowledgements

This work is supported by Swedish Research Council, Swedish Energy Agency, Ångpanneföreningen's Foundation for Research and Development, J. Gust. Richert Foundation, and China Scholarship Council. The authors would like to thank to Dr. Francisco Martinez at the MAX IV Laboratory for support with the synchrotron radiation powder X-ray diffraction measurements. Chao Xu is also gratefully acknowledged for the XPS measurements.
Reference:


Supplementary Information

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$$R \ (\%) = \frac{W'_{Li_2O_2}}{W_{Li_2O_2}} \times 100\% = \frac{W'_{Li_2O_2}/W_{Si}}{W_{Li_2O_2}/W_{Si}} \times 100\% = \frac{(\frac{W'_{Li_2O_2}}{W_{Si}})/(\frac{W_{Si}}{W_{Si}})}{(\frac{W_{Li_2O_2}}{W_{Si}})/(\frac{W_{Si}}{W_{Si}})} \times 100\% = \frac{F_{Li_2O_2}'}{F_{Si}'} \times 100\% \quad (S1)$$

where $W_{Si}$ is Si weight in the electrode, which is not changed during the changing process. $W_{Li_2O_2}$ and $W'_{Li_2O_2}$ are the Li$_2$O$_2$ weights before and after charging process, respectively. $F_{Si}$ and $F_{Li_2O_2}$ are the Si and Li$_2$O$_2$ weight fractions before the charging process, respectively, while $F'_{Si}$ and $F'_{Li_2O_2}$ are the Si and Li$_2$O$_2$ weight fractions after the charging process, respectively.
The residual Li$_2$O$_2$ ratios for the electrodes with 2, 4, and 8 wt% representative catalyst (2 wt% Ru/MNT) after charging for 15 h at a constant current density of 40 mA·g$^{-1}$Li$_2$O$_2$.

The influence of the electrocatalyst amount on the Li$_2$O$_2$ degradation was investigated by adjusting the weight ratio of electrode components and the residual Li$_2$O$_2$ ratios for different electrodes after 15 h of charging were calculated from in situ XRD results (Figure S1). The residual Li$_2$O$_2$ ratios for the electrodes with 2, 4, and 8 wt% catalyst (2 wt% Ru/MNT) charged at a constant current density of 40 mA·g$^{-1}$Li$_2$O$_2$ were 77.9 %, 55.8 %, and 51.4 %, respectively, and the latest is close to the theoretical value (49.2 %) calculated from the charge capacity. Therefore, it can be well established that the cell with 8 wt% electrocatalyst exhibited the highest OER efficiency.

\[ R'_{Li_2O_2} = R_{Li_2O_2} - kt \]  
(S2)

where $R_{Li_2O_2}$ and $R'_{Li_2O_2}$ are the residual Li$_2$O$_2$ ratios before and during the charging time $t$ (h), respectively, and $k$ (h$^{-1}$) is the pseudo-zero-order decomposition rate constant.
Figure S2. The profile for a Li-O$_2$ cell without pre-filled Li$_2$O$_2$ during the charging for 10 h at a constant current density of 70 mA g$^{-1}$carbon.

In order to investigate the charge potential for the side reactions to occur in a Li-O$_2$ cell, we prepared a reference electrode that consisted of Super P, 2 wt% Ru/MNT, Kynar 2801 binder, and Si in a weight ratio of 75:8:7:10 (without Li$_2$O$_2$). As seen in Figure S2, it exhibited a charge plateau around 4.4 V. This plateau represents the potential for the side reaction to occur during battery charge.

Figure S3. The curves (---) and corresponding linear curve fittings (cyan line) of Li$_2$O$_2$ decomposition for the Li-O$_2$ cells with (a) MNT, (b) 0.5 wt% Ru/MNT, (c) 2 wt% Ru/MNT, and (d) home-made Ru nanoparticles charged at a constant potential of 4.3 V during the operando SR-PXD measurements.
Figure S4. The curves (---) and corresponding linear curve fittings (cyan line) of Li$_2$O$_2$ decomposition for the Li-O$_2$ cells with 2 wt% Ru/MNT charged at constant potentials of (a) 4.1 V, (b) 4.3 V, and (c) 4.5 V during the operando SR-PXD measurements.

$k_{4.1V} = 2.4217$ h$^{-1}$

$k_{4.3V} = 11.6391$ h$^{-1}$

$k_{4.5V} = 6.6829$ h$^{-1}$