Systematic Study on the Discharge Product of Pt-Based Lithium Oxygen Batteries

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ABSTRACT: Lithium oxygen batteries have attracted much attention due to the high theoretical energy density. However, they suffer a large overpotential during oxygen evolution process and thus catalysts play a vital role in the reaction. Here, we systematically explored the influence of Pt-based nanoparticle catalysts on the discharge product Li_2O_2 . Because of the superior electrical conductivity and the strong binding with oxygen, Pt-based nanoparticles serve as active sites which are favorable for the growth of toroidal Li_2O_2 . We also found that the content and composition of Pt-based nanoparticle catalysts exert a significant influence on the electrochemical performance of lithium oxygen batteries. The discharge products are composed of crystalline Li_2O_2

and oxygen-rich Li_2O_2 characterized by high-energy X-ray diffraction and Raman. Atomic force microscopy further provides detailed information of the particle size and surface roughness. The loading of Pt catalysts determines the phase and size of Li_2O_2 on the discharged electrode surface. This study will be beneficial for the optimization of Pt-based catalysts used in non-aqueous lithium-oxygen batteries.

Keywords: Lithium- O_2 batteries; Pt-based catalysts; Ru; Discharge products Li_2O_2 ; Atomic Force Microscopy

1. Introduction

Rechargeable non-aqueous lithium oxygen ($\text{Li}-\text{O}_2$) batteries are considered one of the most promising systems to meet the current stringent requirements for power sources because of their extremely high theoretical specific energy, reaching to ten times higher than that of metal-ion batteries.[1-4] However, their performance has been largely limited by the high charge overpotential, resulting in a low round-trip efficiency and side reactions. The excessive charge potential is primarily induced by the undesirable discharge product Li_2O_2 , which accumulates on the surface of the cathode during discharge. To reduce the large overpotential, common strategies include optimizing the porous and conductive supporting carbon materials and applying catalysts for oxygen evolution reaction (OER) in the air electrode.[1, 5, 6]

Recent works have shown that catalysts could greatly reduce the charge voltages of $\text{Li}-\text{O}_2$ batteries. Great efforts have been devoted to developing cathode catalysts, such as noble metals, alloys, metal oxides, and functional doped-carbon materials.[7-14] Among the catalysts, platinum based catalysts show outstanding catalytic activity, attracting much attention of researchers.[7, 15-19] Li et al.[18] fabricated the self-standing composites of Pt/CNTs supported on nickel foam as the cathode for lithium- O_2 batteries. The high catalytic activity of Pt nanoparticles and the unique binder-free architecture endows $\text{Li}-\text{O}_2$ batteries with a high specific capacity, decent rate capability, and good cycle stability. Yang group[16, 19] examined the OER activity of Pt-Au particles supported on carbon as a cathode in lithium- O_2 batteries. The charge voltages ranged from 3.4 to 3.8 V, which were slightly lower than that obtained with Pt. These studies prove that the noble metal catalysts are beneficial to achieving high energy density in $\text{Li}-\text{O}_2$ batteries.

Although it has been demonstrated that the bulk Li_2O_2 could electrocatalytically be decomposed at the presence of catalysts[20], the role of Pt based catalysts has not been fully understood. The crystal structure and morphology of the discharge product (Li_2O_2) have great impacts on the cell performance. Prior researches[21-24] indicated that noble metal catalysts contribute to the formation of poorly crystallized Li_2O_2 . The amorphous Li_2O_2 , for example, improves the reversibility during charge/discharge because it has lower charge overpotential than large toroidal or dish-like products. Therefore, it is important to examine the correlation between catalysts and the discharge products.

In this study, we investigate the effect of a series of Pt-based nanoparticle catalysts with different contents and compositions on Li-O₂ batteries. With multiple techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), high-energy X-ray diffraction (XRD), and Raman spectroscopy, the discharge products on the surface of electrodes were carefully examined. As a comparison, Ru is also introduced to the Pt system as Pt-Ru catalysts to be applied in Li-O₂ batteries. Compared with the monometal catalyst, Ru in Pt-Ru catalyst contributes to the production of more poorly crystalline Li_2O_2 on the surface, especially during the initial discharge stage. The Pt-Ru exhibits superior OER catalytic activity than the Pt noble metal, as determined by an electrochemical test. We also confirm that the content and size of Pt-based nanoparticle catalysts result in different morphologies (diameter and thickness) of toroidal discharge products, as observed by the techniques of SEM and AFM.

2. Experimental Section

2.1 Preparation and Electrochemical Evaluation of Pt/C Cathodes

The Pt-based catalysts studied here are 10 wt% Pt, 40 wt% Pt, and 20 wt% Pt/10 wt% Ru on Vulcan carbon (XC-72), all of which were purchased from Premetek (Wilmington in the state of Delaware, USA). The preparation of cathode was as follow: a mixture containing 80 wt% of Pt-based catalysts on Vulcan carbon and 20 wt% of polyvinylidene fluoride (PVDF) was well mixed by grinding and then pressed onto carbon paper which served as a current collector. Then the cathodes were dried at 80°C under vacuum for 24 h before use. The loading density of active material was approximately 1.0 mg/cm². 1 M lithium trifluoromethanesulfonate (LiCF_3SO_3) in tetraethyleneglycol dimethyl ether (TEGDME) was employed as electrolyte, which was prepared in an argon(Ar) filled glove box at water and oxygen contents below 0.1 ppm.

The electrochemical test was carried out using a Swagelok-type cell, composed of a lithium metal tablet as anode, one slice of glass fiber separator (Fisher Scientific, Pittsburgh in the state of Pennsylvania, USA), 1 mL electrolyte, and a prepared cathode (11 mm diameter). The cells were sealed except for the Al grid window, which exposed the porous cathode to pure oxygen. The batteries were also assembled in the argon filled glove box. Before measurements, the batteries were flushed with pure oxygen for 30 min. Then each measurement started after a 5h open circuit potential step to assure equilibrium in the cell. The electrochemical measurements were carried out using a MACCOR cycler. The discharge-charge performance was conducted in the voltage range of 2.0–4.5 V or at limited capacities (500 mAh/g, 1000 mAh/g) at a constant current of 100 mA/g. We normalized the observed capacity by the weight of the carbon and catalyst for comparison in this study.

2.2 Characterization

Electron microscopy. Field-emission SEM (Hitachi S-4700) was employed to determine the morphology of the discharge product Li_2O_2 . Before the measurements, the discharged cathode was removed from the cell and washed with dimethyl glycol solvent in a glove box. JEOL JEM-ARM200CF with a 200 kV cold field-emission source was employed to evaluate the morphology and particle size of the Pt and Pt-Ru catalysts. An Oxford X-max 100TLE windowless SDD X-ray detector was used for chemical composition analysis. To prepare the TEM specimens, a dilute suspension was prepared by ultrasonically dispersing the Pt catalyst in isopropanol alcohol for 5 min, and a drop of the suspension was placed onto a copper grid and dried.

AFM. The electrodes disassembled from the lithium-oxygen batteries after discharge were characterized by multimode AFM (Bruker Corporation, Digital Instrument, Controller IV) in an Ar-filled glovebox. The particle size and surface roughness (R_q) of Li_2O_2 were obtained by the software V720. R_q is the standard deviation of the Z values within the box cursor and is calculated as:

$$R_q = \sqrt{\sum \frac{(Z_i)^2}{N}},$$

where Z_i is the current Z value and N is the number of points within the box cursor.

High-energy XRD. The cathode laminates after discharge were characterized by high-energy synchrotron XRD to determine the formation of Li_2O_2 , which was carried out at the 11-ID-C beamline of the Advanced Photon Source, Argonne National Laboratory. The X-ray wavelength was 0.11798 Å. The samples were completely sealed by Kapton tape as a protective film in the glove box to avoid any side reactions from air. The XRD patterns were collected in transmission mode using a PerkinElmer large-area detector. The collected two-dimensional patterns were then integrated into conventional one-dimensional patterns (intensity versus 2θ) for final data analysis using Fit2d software.

Raman spectra. The Raman spectra of discharged cathodes were obtained using a Renishaw 2000 or inVia microscope spectrometer with a HeNe laser at an exciting wavelength of 633 nm. The sample was loaded inside a glove box to a gas-tight Raman cell with a glass or quartz window. The Raman spectrum collection was performed in 180° reflective mode. Roughly 10% of the maximum 13 mW laser intensity was applied.

3. Results and discussion

Various Pt-based catalysts (Pt1 - 10 wt% Pt, Pt2 - 40 wt% Pt, Pt3 - 20 wt% Pt and 10 wt% Ru on Vulcan carbon) were investigated here. Transmission electron microscopy (TEM) images show that Pt and Pt-Ru nanoparticles are uniformly distributed on graphite carbon (Figure 1a–c), and the particle size of Pt2 (~4 nm) is apparently larger than those of Pt1 and Pt3 (~2 nm). In such a small range, Pt and Ru atoms are distributed uniformly within individual particles, indicating the alloying of Pt and Ru; these results are supported by energy-dispersive X-ray mapping (Figure 1d–e).

Figure 1. (a, b, c) TEM images of Pt1, Pt2, and Pt3, respectively. (d) High angle annular dark field (HAADF) image of Pt3 with the corresponding elemental mappings shown in (e) for Pt, and (f) for Ru.

The discharge and charge profiles of Pt-based catalysts were recorded at 100 mA/g in the voltage range of 2.2–4.5 V vs. Li^+/Li , as shown in Figure 2a. The discharge capacities of Pt1 and Pt3 electrodes are much higher than that of Pt2, and the Pt3 electrode exhibits the lowest charge overpotential. This indicates that the content and composition of Pt-based catalysts exert a noticeable influence on the electrochemical performance of Li-O₂ batteries. And the results show that the nanoscale Pt-based particles, distributed evenly on supporting materials, are better catalysts in Li-O₂ batteries than the large agglomerated ones. The deep discharged electrodes were examined by SEM as shown in Figure 2b–d. The discharge products covered on the surface of electrodes are primarily toroidal particles. However, the sizes (diameter and thickness) are different based upon loading and type of catalyst. The diameters of the toroidal discharge products of Pt2 are obviously smaller than the others. Carl's group[25] reported that the large facets of Li₂O₂ plates formed the toroidal particles and the plate spraying may be attributed to the difference in surface stress driving the evolution from disc to toroidal shapes. The Pt nanoparticle catalyst loading of Pt2 is much more than those of Pt1 and Pt3, suggesting more active sites with strong oxygen binding for discharge. Therefore, smaller toroidal discharge products are covered on the surface of the Pt2 electrode, comparing with the other two.

Figure 2.(a) First galvanostatic discharge/charge curves of Pt1, Pt2, and Pt3 at 100 mA/g in the voltage range of 2.2–4.5 V. SEM images of electrodes discharged to 2.2 V at 100 mA/g: (b) Pt1, (c) Pt2, and (d) Pt3.

To investigate the catalytic activity for OER kinetics, the first charge voltages were compared under capacity-controlled conditions at the same rate (100 mA/g), as shown in Figure 3a–b. The mid-capacity potential (defined as the potential at half capacity,[15] 3.7 V) of Pt3 is obviously lower than those of Pt1 and Pt2 (4.1 V and 4.2 V), and the onset oxidation potential of Pt3 (3.0 V) is also lower than those of Pt1 and Pt2 (both 3.2 V) at a fixed capacity of 500 mAh/g. All these performances indicate the superior electrocatalytic activity for OER of the Pt-Ru catalyst compared with the Pt noble metal. At the capacity limit of 1000 mAh/g, the mid-capacity potential of Pt2 is barely changed, while that of Pt1 slightly shifts to 4.2 V. Meanwhile, the mid-capacity potential of Pt3 significantly increases to 3.9 V. The corresponding electrodes discharged with capacities of 500 mAh/g and 1000 mAh/g at current density of 100 mA/g were investigated by SEM, Raman spectroscopy, and XRD. In Figure 4, compared with the fresh cathodes, toroidal or dish-like discharge products begin to emerge at the fixed capacity of 500 mAh/g. It should be noted that the discharge products of the Pt2 grow more quickly to the large toroidal ones than the others. When the discharge capacities reach 1000 mAh/g, more toroidal discharge products are covered on the surface of the Pt2 electrode, but their sizes only slightly change. Meanwhile, the

discharge products of Pt1 and Pt3 evolve to large toroidal shapes with many plate-like arrays. However, there are fewer discharge products on the surface of the Pt3 electrode than the others. This may imply that the different morphology evolution of discharge products results in the mid-capacity potential change, as mentioned above.

Figure 3. First galvanostatic charge curves of Pt1, Pt2, and Pt3 at 100 mA/g with capacities of (a) 500 mAh/g and (b) 1000 mAh/g. XRD spectra of electrodes discharged with different capacities at 100 mA/g current: (c) Pt1, (d) Pt2, and (e) Pt3.

The XRD and Raman spectrum characterized the discharge products at fixed discharge capacities of 500 and 1000 mAh/g. The peaks from the discharged electrodes are identified as the (100), (101), and (110) peaks of Li₂O₂ according to the standard XRD histogram, [8, 26, 27] as shown in Figure 3c–e. XRD analysis confirms that the discharge products are mostly crystalline Li₂O₂. Compared with electrodes Pt1 and Pt2, the Li₂O₂ peak intensity of Pt3 is extraordinarily weaker at the fixed discharge capacity of 500 mAh/g, indicating the poorly crystallized Li₂O₂ of Pt3. When the discharge capacity increases to 1000 mAh/g, the Li₂O₂ peak intensity of Pt3 becomes much stronger. This result suggests more crystalline Li₂O₂ emerge on the surface of Pt3 electrode at the fixed discharge capacity of 1000 mAh/g, which may be the reason that the mid-capacity potential becomes larger with the capacity increasing in Pt3 system. In the Raman

spectra of the discharged electrodes (Figure 5), the peaks near 1600 cm^{-1} and 1340 cm^{-1} are from the graphite (G, internal phenyl ring stretch) band and disordered graphitic islands (D band), respectively.[28, 29] The band located near 1123 cm^{-1} is a signature of LiO_2 -like components, and the band near 1505 cm^{-1} has been identified to come from strong interactions between LiO_2 and a graphite carbon surface.[20, 30, 31] Accompanied by the capacity increase, the relative peak intensities of LiO_2 become stronger because of the accumulation of discharge products. We can therefore conclude that the toroidal discharge products of Pt1 and Pt2 are made up of LiO_2 -like species and Li_2O_2 components, as reported before.[31] However, we also surmise that the 10 wt% Ru in Pt-Ru may result in the different shape evolution of discharge products between Pt3 and the others. Recently, numerous studies have reported the role of Ru-based catalysts in transforming the morphology and structure of discharge products in lithium- O_2 batteries.[9, 21, 24, 32-34] The Ru-based catalysts promote the formation of Li_2O_2 films (lithium-deficient $\text{Li}_{2-x}\text{O}_2$) with poor crystal structure on the surface of the electrode, and lithium-deficient $\text{Li}_{2-x}\text{O}_2$ have been reported to have much lower overpotentials than large toroidal crystal Li_2O_2 during charging.[21, 23, 25, 35, 36] Therefore, the lower charge overpotential of the Pt-Ru catalyst compared with the Pt-only system is caused by the introduction of Ru nanoparticles. Furthermore, the capacity versus cycle number plots of Li- O_2 batteries with Pt1, Pt2 and Pt3 catalysts are shown in Figure 6. The results demonstrate that the Li- O_2 battery with Pt-Ru catalyst shows better cycling performance than the others, indicating its better stability.

Figure 4. SEM images of Pt1, Pt2, and Pt3 electrodes: (a, d, g) pristine electrodes before cycling, (b, e, h) after discharge with 500 mAh/g capacity at 100 mA/g current, and (c, f, i) after discharge with 1000 mAh/g capacity at 100 mA/g current. Red scale bar = 1 μm .

Figure 5. Raman spectra of electrodes discharged with different capacities at 100 mA/g current: (a) Pt1, (b) Pt2, and (c) Pt3.

To provide straightforward and detailed information, we observed the discharge products using AFM (Figure 7). Through the AFM images (tapping mode, providing topography, and phase images), we can clearly see that the toroidal discharge particles are composed of arrays of plate-like products, especially in Figure 7b. The thicknesses of the Li_2O_2 plates are all in the range

of 50–150 nm. The diameters and thicknesses of the toroidal particles of Pt1 and Pt3 are around 500 nm and 350 nm, respectively, while those of Pt2 are approximately 250 nm and 250 nm, respectively. Meanwhile, the surface roughness (R_q) of the Li_2O_2 of Pt1 and Pt3 is approximately 25 nm, while that of Pt2 is approximately 15 nm, further demonstrating the difference in morphology. The surface roughness implies that the toroidal Li_2O_2 of Pt2 is composed of fewer layers of plate-like Li_2O_2 crystallites than the others.

Figure 6. The discharge and charge capacity versus cycle number of lithium- O_2 batteries with Pt1, Pt2 and Pt3 as cathodes at current densities of 100 mA/g by curtailing the capacity to 1000 mAh/g in the voltage range of 2.2–4.5 V.

Figure 7. AFM images of electrodes discharged at 100 mA/g current: (a) Pt1, (b) Pt2, and (c) Pt3.

4. Conclusion

Through the characterization and discussion provided above, we can conclude that the content and composition of Pt-based catalysts exert a significant influence on the morphology and structure of the discharge product Li_2O_2 . The Pt-based nanoparticles, as active sites, are favourable

for the growth of toroidal Li_2O_2 because of their strong binding with oxygen. The content and the size of Pt nanoparticles also affect the electrochemical performance, and the nanoscale Pt particles, distributed evenly on supporting materials, are better catalysts in lithium- O_2 batteries than the large agglomerated ones. Compared with pristine Pt nanoparticle catalysts, the mid-capacity charge voltage could be reduced when Ru is added to the noble metal Pt as a Pt-Ru catalyst, which is attributed to the role of Ru in promotion of poorly crystallized Li_2O_2 discharge products. The AFM results provide more detailed information about the particle size and surface roughness of the discharge product Li_2O_2 , which is a new characterization method applied in lithium- O_2 batteries. This study will contribute to the adoption and optimization of Pt-based catalysts used in non-aqueous lithium- O_2 batteries.

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