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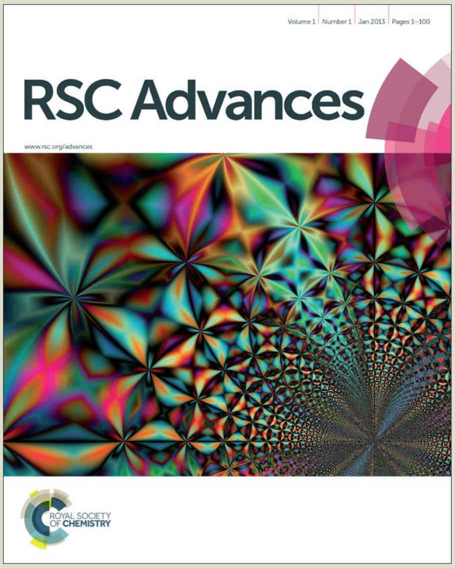

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In situ Synthesis of Amorphous RuO_2/AZO as a Carbon-Free Cathode Material for Li-O_2 Batteries

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The composite of amorphous RuO_2 as an electrocatalyst and aluminum-doped ZnO (AZO) as a cathode material were combined and developed into a carbon-free cathode material for Li-O_2 batteries for the first time. The amorphous RuO_2/AZO carbon-free cathode exhibits a noticeably reduced overpotential as well as an enhanced specific capacity.

Despite the enormous energy density of Li-O_2 batteries, which is 3-5 times greater than that of Li-ion batteries[1], they are associated with known limitations, such as degradation of the electrolyte, poor cycle stability, and a low round-trip efficiency, among others.[2] Among these shortcomings, the formation of lithium carbonate (Li_2CO_3) is one of the main problems leading to the deterioration of the electrochemical properties of Li-O_2 batteries. Because carbon is the most commonly used cathode material, lithium carbonates are produced and deposited onto the surface of the cathode during discharge process and do not easily decompose during the charge process. As a result, the available pores on the cathode are blocked, leading to capacity fading during cycling. The formation of lithium carbonates is based on the carbon cathode and on electrolytes to form a Li_2CO_3 layer at the interface between the carbon cathode and the Li_2O_2.[3] In addition, Li_2CO_3 decomposes into CO_2 gas at the end of charge process.[4] Consequently, preventing the formation of lithium carbonate must be done to enhance the electrochemical properties, which is why conductive oxides are considered as a cathode material. Li *et al*. reported that Ru/ITO can be applied as a carbon-free cathode material for Li-O_2 batteries owing to its excellent electrochemical properties, such as its much lower charging overpotential and better cyclability.[5] Aluminum-doped ZnO (AZO) has also been reported as a cathode material by our group, and the electrochemical performances of AZO/Ru were investigated with the suppression of Li_2CO_3 formation confirmed. In this study, we employed RuO_2 as an electrocatalyst and AZO as a cathode material. AZO is chemically and physically stable and is much less expensive than indium-based conductive oxide. The electrical conductivity of AZO was increased by doping Al^{3+} onto Zn^{2+} sites, contributing to the number of electrons involved in the electron formation process by means of the interstitial zinc atoms and the oxygen vacancies.[6] However, despite the fact that these materials show electrochemical activity toward Li-O_2 batteries, there are additional steps needed to introduce an electrocatalyst onto cathode materials in this case. Therefore, to reduce the number of synthesis steps and to enhance the electrochemical performance levels of the carbon-free cathode material, we developed an in situ microwave-assisted hydrothermal method, which has benefits such as a simple and facile reaction process, a low reaction temperature, and the realization of uniformity in the products, as the reaction occurs at the molecular level.[7] In addition, the contact between the electrocatalyst RuO_2 and the cathode material AZO can be enhanced by the in situ synthesis approach due to the direct reaction among the starting materials. In preparing the RuO_2/AZO, the crystallinity was controlled by varying the annealing temperature, after which the corresponding electrochemical performances were examined.

RuO_2/AZO was synthesized with a microwave-assisted hydrothermal method by reacting aluminum nitrate nonahydrate, zinc nitrate hexahydrate and ruthenium chloride hydrate (for detailed synthesis method, please see the electronic supplementary information (ESI†)). The precursor powder was annealed at temperatures of 350, 400, and 500°C in an oxidative atmosphere to obtain the RuO_2/AZO powder.

The crystal structures of the synthesized RuO_2/AZO particles were studied. Fig 1 shows the XRD patterns of RuO_2/AZO corresponding to the annealing temperature, which ranged from 350°C to 500°C in this study. All samples annealed at a given temperature include diffraction patterns representing zinc oxide (JCPDS#01-070-2551). However, the annealing temperature affected the diffraction patterns of the RuO_2. The RuO_2/AZO particles annealed at 400 and 500°C include diffraction patterns corresponding to RuO_2 (JCPDS#01-071-4825), showing the formation of a crystalline phase, whereas those annealed at 350°C show no diffraction patterns except for zinc oxide, thus expressing the amorphous nature of RuO_2. Therefore, RuO_2/AZO annealed at 350°C is a composite of amorphous RuO_2 and crystalline AZO, while others are composites of both crystalline RuO_2 and AZO.

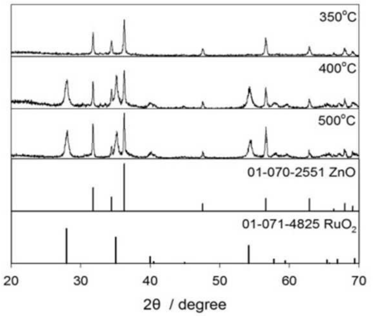

Fig. 1 XRD patterns corresponding to the annealing temperature

The microstructural characteristics of the RuO$_2$/AZO prepared at different temperatures were observed by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) mapping. As shown in the TEM images (Fig. S1 in ESI†), all of the particles of RuO$_2$/AZO prepared at different temperature are composed of nanorods with a diameter of about 20 nm and nanoparticles with diameters of several nanometers. The EDS mapping was carried out on these particles to clarify the distribution of each element (Fig. 2). The signals of Al, Zn and Ru, represented as bright colored spots, were noted, and all of the elements were found to be well distributed within the particles. However, the mapping images taken from both nanorods and nanoparticles indicate the different contribution of the elements. In the nanorod-region, only blue spots, which correspond with the Ru element, were observed, whereas the red and green spots correspond with Al and Zn were not detected. In addition, the mainly distributed elements in the nanoparticle-region were Al and Zn. Considering the XRD results in Fig. 1, it can be concluded that the nanoparticles and nanorods correspond to AZO and RuO$_2$, respectively, and both materials are evenly mixed. Therefore, unlike the RuO$_2$/AZO prepared at temperatures greater than or equal to 400°C, resulting in a microstructure of both crystalline RuO$_2$ and AZO, the RuO$_2$/AZO prepared at 350°C is composed of amorphous RuO$_2$ and crystalline AZO.

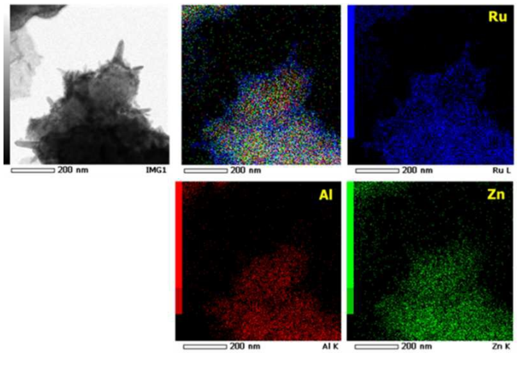

Fig. 2 TEM/EDS mapping images of amorphous RuO$_2$/AZO

Because the electrochemical properties of Li-O$_2$ batteries strongly depend on the surface properties, such as the surface area and pore volume, the Brunauer-Emmett-Teller (BET) technique was employed (Table S1 in ESI). According to the results, the surface area and pore volume of RuO$_2$/AZO gradually increased as the annealing temperature was increased. The amorphous RuO$_2$/AZO has a surface area of 17.1 mg^2/g and a pore volume of 0.046 cm^3/g, whereas all of the crystalline RuO$_2$/AZO samples have values which are higher than this, indicating that the amorphous RuO$_2$/AZO has the poorest surface properties among all of the synthesized samples. In general, a high surface area and a large pore volume are favorable, as a high internal surface area can provide numerous reaction sites for oxidation and reduction, a condition which is advantageous for increasing the specific capacity. Moreover, a large pore volume can reduce the blockage of the available pores caused by the deposition of ORR products, resulting in improved electrochemical performance.[8] In addition, many researchers have reported that the electrical conductivity of AZO is highly dependent on the annealing temperature, and that with an increase in the annealing temperature, the electrical conductivity can be improved at temperatures up to 500°C. Judging by these factors, annealing materials at low temperatures would not be preferred for cathode materials. However, the electrochemical properties of RuO$_2$/AZO were contrary to our expectations. The voltage profiles of amorphous and crystalline RuO$_2$/AZO prepared at diverse temperature are shown in Fig. 3. The amorphous RuO$_2$/AZO shows improved performance compared to the crystalline RuO$_2$/AZO, exhibiting a specific capacity of 1040 mAh/g and an overpotential of 0.8 V. With an increase in the annealing temperature, the electrochemical performance levels of RuO$_2$/AZO deteriorate. The specific capacity of the crystalline RuO$_2$/AZO prepared at 500°C dropped significantly to 830 mAh/g with an increment in the overpotential of 1.0 V. Despite the fact that the specific capacity and discharge overpotential of the crystalline RuO$_2$/AZO annealed at 400°C are equal to those of the amorphous RuO$_2$/AZO, the charge overpotential is much higher, resulting in a total overpotential of 1.2 V. This is because the catalytic activity of amorphous RuO$_2$ toward OER is higher than that of crystalline RuO$_2$. Consequently, it can be concluded that amorphous RuO$_2$/AZO offers better electrochemical properties compared to those of crystalline RuO$_2$/AZO, despite the fact that the properties of AZO, such as the BET surface properties and electrical conductivity, cannot meet the required specifications. This countertrend can be explained by the use of the electrocatalyst RuO$_2$. It can be deduced that the catalytic activity of RuO$_2$ is associated with crystallinity of the material. The catalytic activity of amorphous RuO$_2$ is higher than that of crystalline RuO$_2$, and it diminishes with an increase in the crystallinity. Therefore, it can be assumed that in certain materials such as AZO, the electrochemical properties of Li-O$_2$ batteries are strongly influenced by the electrocatalyst and the catalytic effect is dominant over the properties of the cathode materials.

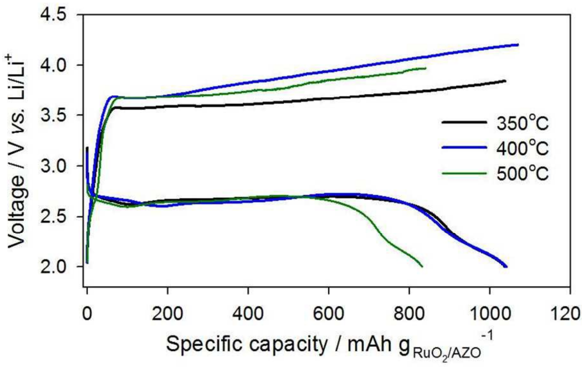

Fig. 3 Voltage profiles of RuO$_2$/AZO corresponding to the annealing temperature

The reversible formation and decomposition of the oxygen reduction reaction (ORR) products on the surface of the amorphous RuO_2/AZO were investigated by field-emission scanning electron microscopy (FE-SEM) and by an X-ray photoelectron spectroscopy (XPS) analysis. Fig. 4 shows FE-SEM images of the as-prepared amorphous RuO_2/AZO, after the first discharge and after the first charge. Each electrode was washed with dimethyl ether (DME) in order to remove any residual Li salt from the electrolyte. As shown in Fig. 4(b), ORR products were deposited onto the surface of the amorphous RuO_2/AZO after a full discharge, as confirmed by the Li 1s and O 1s XPS spectra shown in Fig. S2. A binding energy peak of about 55 eV in the Li 1s spectrum and 531.5 eV in the O 1s spectrum represent the presence of Li_2O_2. A reversible reaction was observed, in that the peak corresponding to Li_2O_2 disappeared in the Li 1s and O 1s spectra after the first charge. This is strongly supported by the FE-SEM image in Fig. 4(c), in which all of the ORR products deposited onto the surface of the cathode materials were completely decomposed after the first charge. Therefore, amorphous RuO_2/AZO is electrochemically active toward the formation and decomposition of Li_2O_2 on the cathode surface, which is a fundamental redox reaction in Li-O_2 batteries. Moreover, the reaction is reversible.

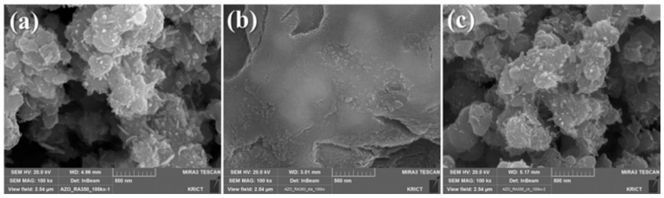

Fig. 4 FE-SEM images of amorphous RuO_2/AZO: (a) pristine (b) after the first discharge (c) after the first charge

4. Conclusion

In summary, amorphous RuO_2/AZO was synthesized by a microwave-assisted hydrothermal method and developed as a carbon-free cathode material for Li-O_2 batteries for the first time. The composite of the electrocatalyst RuO_2 and cathode material of AZO was fabricated in an in situ synthesis, which offers a simple, rapid, and cost-effective method, as additional steps are not needed. The crystallinity of RuO_2 has a strong effect on the catalytic activity in Li-O_2 batteries. The catalytic activity of RuO_2 was increased in conjunction with decreased crystallinity, indicating that amorphous RuO_2 can be considered to be the most effective electrocatalyst with AZO. As a carbon-free cathode with RuO_2/AZO, the electrochemical properties were significantly affected by RuO_2 as compared to AZO, signifying that the catalytic activity has a dominant effect on Li-O_2 batteries with certain materials, such as AZO in this case. Further studies are necessary to clarify the role of crystallinity in RuO_2.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, TEM images, XPS analysis, BET analysis]. See DOI: 10.1039/c000000x/

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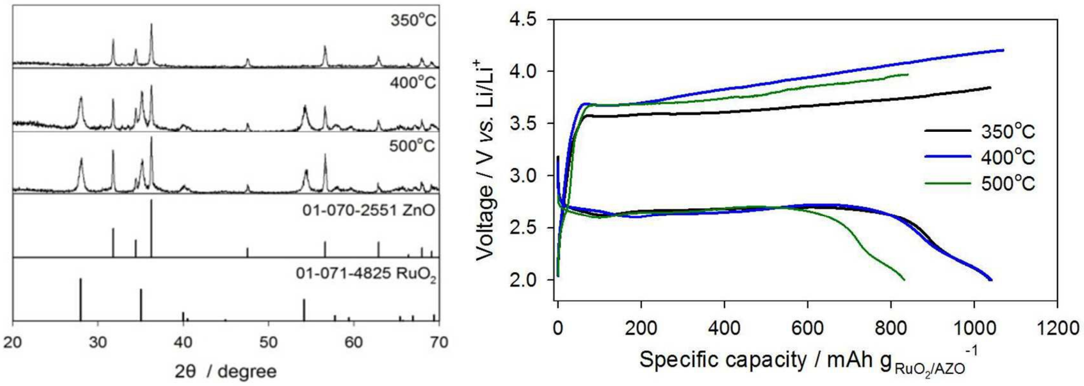
Graphical Abstract



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