

Al-doped Ceria: A New Cathode Catalyst for Li–O₂ Batteries

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(Received April 2, 2012; CL-120286; E-mail: parkcj@jnu.ac.kr)

Nanostructured aluminum-doped ceria (ADC) particles with uniform spherical shape, as a new catalyst material for the cathode in Li–O₂ batteries, are prepared by a solution combustion method. The nonaqueous Li–O₂ cell employing the Ce_{0.8}Al_{0.2}O₂ catalyst exhibits a specific capacity as high as 1549 mA h g⁻¹. The discharge product of the Li–O₂ cell mostly contains lithium carbonate and a small amount of lithium peroxide.

Researchers have tried to incrementally improve the electrode materials used in Li ion batteries, in hopes that the batteries can reach their theoretical capacities while maintaining acceptable charge and discharge rates.¹ However, it is now believed that the current technology has reached its limit in incremental improvement with respect to energy density, although it is still insufficient to satisfy the requirements of electric vehicles. Hence, a new battery technology based on new cell chemistries, novel processing, and flexible manufacturing is urgently needed.

A Li–O₂ electrochemical couple, with the oxygen being free and lithium of great gravimetric capacity, appears very attractive.^{2,3} Rechargeable Li–O₂ batteries promise up to threefold higher specific energy than conventional Li ion batteries. However, a Li–O₂ battery is still far from being a practical technology because of its many difficulties, such as cyclability, rate capability, and lifetime.^{2,4,5} Hence, it is important to find a suitable electrocatalyst³ that can break the strong oxygen–oxygen bond and then reform them to improve cell performance. Especially rare earth CeO₂ is of particular interest due to its environmentally friendliness, high oxygen-transfer ability, electrochemical redox characteristics,⁶ and much lower price than noble metal catalysts.

In this study, Al-doped ceria (ADC) was synthesized and studied as a new catalyst material for the cathode of the Li–O₂ battery.

A novel and simple solution combustion synthesis technique was used to prepare the aluminum-doped ceria. Nitrate precursors of aluminum and cerium were dissolved in deionized water, and an adequate amount of oxidizer i.e. glycine was added during stirring. Then, the mixture was kept in a preheated furnace at 300 °C until the end of the combustion process. The formed materials were characterized by X-ray diffractometer (XRD), transmission electron microscopy (TEM), and Brunauer–Emmett–Teller (BET) method to analyze structure, morphology, and surface area, respectively. Furthermore, Li–O₂ coin cells were assembled in a glove box by stacking an air electrode containing acetylene black (85 wt %), ADC (10 wt %), and poly(vinylidene difluoride) (5 wt %) on the Ni foam current collector and Li metal foil. Two electrodes were separated by a CELGARD 5500 separator soaked with 1 M lithium bis(tri-

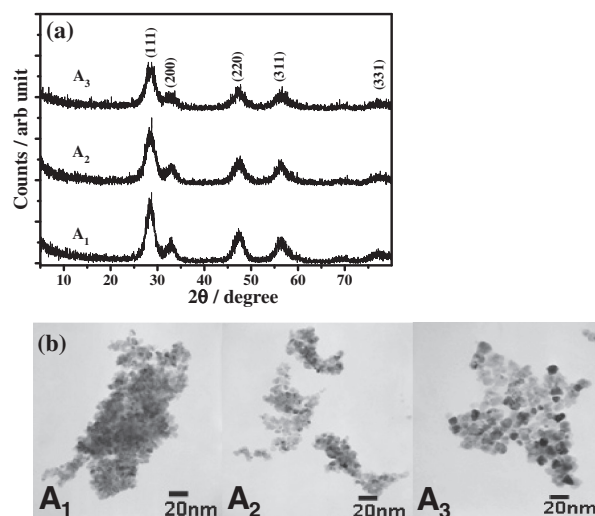


Figure 1. (a) XRD patterns and (b) TEM images of combustion synthesized ADC samples.

fluoromethane)sulfonamide in 1:1 PC/EC. Li–O₂ cells were tested using a Wonatech WMPG 1000 battery cycler. The charge/discharge reaction products of the Li–O₂ cell were analyzed by using XRD, FTIR, and Raman spectroscopy.

The structural analysis of the product obtained from the combustion reaction between nitrate precursors and glycine oxidizer is given in Figure 1a. The powder samples are hereafter named A₁ (Ce_{0.9}Al_{0.1}O₂), A₂ (Ce_{0.8}Al_{0.2}O₂), and A₃ (Ce_{0.7}Al_{0.3}O₂). The broad peaks of the XRD pattern indicate the formation of ADC in the form of nanostructures. The structural calculations using the obtained peaks confirmed the cubic fluorite structure of the ADC. Figure 1b shows the TEM images of the ADC powder samples. The spherical particles with connected morphology were observed for all the three samples. The average particle size measured from the TEM images was 3, 5, and 12 nm for A₁, A₂, and A₃ respectively.

The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface areas of the samples from the N₂ adsorption data. The specific surface areas observed for A₁, A₂, and A₃ were 54.2, 70.4, and 30.4 m² g⁻¹, respectively. The pore sizes obtained from the corresponding NLDFT pore size distribution curves for A₁, A₂, and A₃ were 12, 13.9, and 27.7 nm, respectively. The galvanostatic discharge capacities of the Li–O₂ cells containing the ADC catalysts were determined on the basis of carbon weight. Variation of surface area of the catalyst material and discharge capacity of Li–O₂ cell as a function of doping percentage are shown in Figure 2a. The largest surface area of the catalyst resulted in the highest specific capacity for the A₂ sample due to the efficient O₂ reduction on

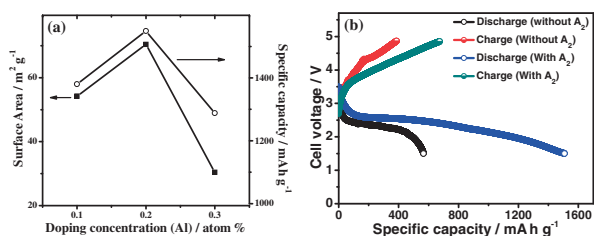


Figure 2. (a) Specific surface area and discharge capacity with Al (atom %) and (b) charge–discharge curve for A₂-catalyzed Li–O₂ cell.

the catalyst surface. The plot reveals that the catalytic efficiency of the ADC was proportional to the surface area of the material. The discharge capacity values obtained for the Li–O₂ cells with A₁, A₂, and A₃ catalysts were 1380, 1549, and 1288 mA h g⁻¹, respectively. A typical charge–discharge curve of Li–O₂ cell with and without catalyst is shown in Figure 2b. From charge–discharge plots, it is observed that the catalyst has improved the performance of the Li–O₂ cell. The charge capacity of the cell was half the discharge capacity. The specific capacity of the cell might have degraded because of the formation of compounds other than Li₂O₂ during the discharge reaction.

To investigate the causes of the capacity degradation, the reaction products of the cell were analyzed systematically. After galvanostatic discharge of the cell, the cathode was analyzed using FTIR in an inert environment. The spectra obtained in the range of 400–1800 cm⁻¹ are shown in Figure 3a. The figure reveals that the dominant product of the discharge reaction was lithium carbonate and not lithium peroxide. The peaks related to C=O and C–O related to lithium formate and lithium acetate are also present. The FTIR data proved that the decomposition of electrolyte took place along with the reaction of Li and oxygen. These results are analogous to the recent reports demonstrating the dominant decomposition of the alkyl carbonate electrolyte in the absence of a catalyst.^{7,8} The data indicate the formations of lithium carbonate and oxides of lithium, so it is difficult to distinguish between lithium oxide and lithium peroxide. Hence, the discharge product was analyzed by FT-Raman because it is sensitive to the presence of Li₂O₂ (Figure 3b). The Raman shift data for the discharge product show the peak near 800 cm⁻¹ revealing the presence of Li₂O₂. In addition a small peak at 1125 cm⁻¹ corresponds to the formation of Li₂O. However, the intensities of the peaks suggest that their amounts were much smaller than that of lithium peroxide. A large peak associated with lithium carbonate is evident near 1100 cm⁻¹. Finally, the discharge products before and after charging the cell were examined by XRD. Figure 3c gives the XRD pattern of the cathode surface before and after charging. The pattern shows peaks related to lithium carbonate and lithium oxide. However, the amount of the carbonate phase was larger than that of lithium peroxide. These results are in close agreement with those reported by Freunberger et al.⁷ After charging, the peaks related to the lithium peroxide vanished and the intensities of the lithium carbonate peaks decreased. This result indicates that the

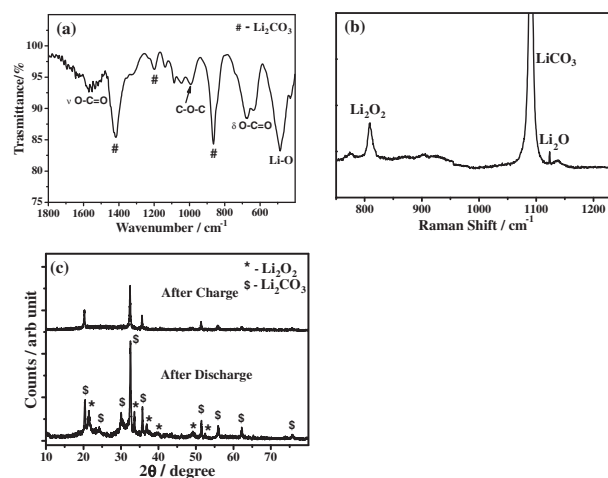


Figure 3. (a) FTIR and (b) Raman spectra of reaction product before charge, (c) XRD pattern of reaction product before and after charge of A₂-catalyzed Li–O₂ cell.

lithium peroxide and the small amount of lithium carbonate decomposed to give oxygen and lithium during the charge process.⁹

In conclusion, Al-doped ceria was successfully prepared by a combustion technique. The maximum discharge capacity of 1549 mA h g⁻¹ was observed for Ce_{0.8}Al_{0.2}O₂, which had higher surface area and highly porous morphology. The discharge product was dominated by lithium carbonate and a small amount of lithium peroxide.

This work was supported by the Energy Efficiency & Resources Program of the Korea Institute of Energy Technology Evaluation and Planning (No. 20112010100110) Grant and the ITRC (Information Technology Research Center) Support Program of the NIPA (National IT Industry Promotion Agency) (No. NIPA-2012-H0301-12-1009), funded by the Korea Government Ministry of Knowledge Economy.

References

- 1 M.-K. Song, S. Park, F. M. Alamgir, J. Cho, M. Liu, *Mater. Sci. Eng., R* **2011**, *72*, 203.
- 2 R. Padbury, X. Zhang, *J. Power Sources* **2011**, *196*, 4436.
- 3 F. Cheng, J. Chen, *Chem. Soc. Rev.* **2012**, *41*, 2172.
- 4 T. Ogasawara, A. Débart, M. Holzapfel, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2006**, *128*, 1390.
- 5 A. Débart, A. J. Paterson, J. Bao, P. G. Bruce, *Angew. Chem., Int. Ed.* **2008**, *47*, 4521.
- 6 Y. Zhou, J. A. Switzer, *J. Alloys Compd.* **1996**, *237*, 1.
- 7 S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2011**, *133*, 8040.
- 8 F. Mizuno, S. Nakanishi, Y. Kotani, S. Yokoishi, H. Iba, *Electrochemistry* **2010**, *78*, 403.
- 9 B. Sun, B. Wang, D. Su, L. Xiao, H. Ahn, G. Wang, *Carbon* **2012**, *50*, 727.