SECM Study of Optimization of the Electrochemical Reaction Mechanism at the Air Cathode for Zinc-Air Secondary Element

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Metal air batteries, due to their features of high theoretical energy density, low cost, increased safety and environmental friendliness, have been considered the promising power source for rapidly developed portable electronic devices and electrified vehicles, and energy storage for the smart grids.[1, 2] Among the suitable metals for metal-air batteries, zinc, due to its advantages of natural abundance, low equilibrium potential, stability in aqueous medium, flat discharge voltage and long shelf-life, has attracted increasing attention in recent years.[3, 4, 5] The development of the rechargeable (secondary) zinc-air batteries is required by the above mentioned applications.[6, 7] The design of the air cathode is of great importance in optimizing the performance of the whole battery system. Different materials and structures of the air cathode, the catalysts loaded and the electrolytes used will all have significant effects on the diffusion and adsorption of the oxygen molecules as well as the reaction intermediates, thus altering the reaction path way in both discharging and charging processes[1, 2]. Scanning electrochemical microscope (SECM) is a powerful techniques to examine electrochemical processes at liquid-solid interface with spatial resolution,[8] which is desirable for studying the reaction mechanism at the air cathode. There have been many reports of studying oxygen reduction on different types of substrates using SECM, for localized detection of the reduction products and intermediates, as well as examination of the reaction kinetics.[9, 10, 11, 12, 13]

Our group investigated the electrochemistry involved in the battery process at the air cathode using advanced scanning electrochemical microscope technique. A special design of SECM measuring head for conducting measurement at gas diffusion electrode under the defined atmosphere has been made for this research purpose. The current studies present characterizations of oxygen reduction on different electrode materials in ionic liquids and alkaline solutions. The study has compared the oxygen reduction, in aqueous alkaline solution, protic ionic liquid, aprotic ionic liquid and ionic liquid mixtures with water in different ratios. The influence of proton and moisture on the reduction pathway of oxygen in ionic liquid has been discussed.

Figure 1. A SECM working station integrated with high speed digital bi-potentiostat (Gamry, US) for the detection of reaction intermediates.

Important parameters, such as diffusion coefficient (*D*), number of transferred electrons (*n*) and the solubility of the oxygen (c^*) in electrolytes of various compositions were determined by an approach combining four simple electrochemical techniques (cyclic voltammetry, chronoamperometry, liner sweep voltammetry at rotating disk electrode and cyclic voltammetry at ultra-microelectrode). Spatially resolved detection of the reaction intermediates, during both discharging (oxygen reduction) and recharging (oxygen evolution) process, is performed using SECM integrated with high scan rate digital bi-potentiostat (Figure 1, 2). In the experiment, the influence of cathode material of different microstructure as well as catalysts of different chemical composition and nanostructure to the formation of intermediates is examined.

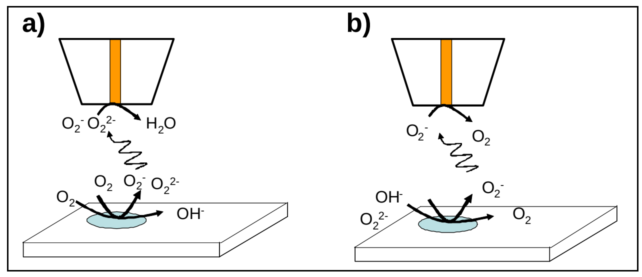

Figure 2. Principle of local detection of soluble reaction intermediates. a) detection of O_2^{2-} und $O_2^{\bullet-}$ from the reduction of oxygen; b) detection of intermediates ($O_2^{\bullet-}$ as an example) in the oxidation of OH^- or peroxides. The scheme is greatly simplified.

In the electrolyte containing zinc ion, the influence of the deposition of discharging product (ZnO) and carbonate (by-product in alkaline electrolyte) to the functioning of the gas diffusion electrode will also be investigated with SECM. The result provides fundamental understanding of the mechanism of the air cathode reactions during discharging and charging battery process, offering guidance on how to systematically improve the performance of the Zinc-air battery.

References

(1) Cheng, F.; Chen, J. *Chemical Society Reviews* **2012,** *41,* 2172-2192.
(2) Lee, J.-S.; Kim, S. T.; Cao, R.; Choi, N.-S.; Liu, M.; Lee, K. T.; Cho, J. *Advanced Energy Materials* **2011,** *1,* 34-50.
(3) Arora, P.; Zhang, Z. M. *Chemical Reviews* **2004,** *104,* 4419-4462.
(4) McLarnon, F. R.; Cairns, E. J. *Journal of the Electrochemical Society* **1991,** *138,* 645-664.
(5) Xianyou, W.; Sebastian, P. J.; Smit, M. A.; Hongping, Y.; Gamboa, S. A. *Journal of Power Sources* **2003,** *124,* 278-84.
(6) Chen, Z.; Yu, A.; Ahmed, R.; Wang, H.; Li, H.; Chen, Z. *Electrochimica Acta* **2012,** *69,* 295-300.
(7) Li, X.; Zhu, A. L.; Qu, W.; Wang, H.; Hui, R.; Zhang, L.; Zhang, J. *Electrochimica Acta* **2010,** *55,* 5891-5898.
(8) Wittstock, G.; Burchardt, M.; Pust, S. E.; Shen, Y.; Zhao, C. *Angewandte Chemie-International Edition* **2007,** *46,* 1584-1617.
(9) Nogala, W.; Burchardt, M.; Opallo, M.; Rogalski, J.; Wittstock, G. *Bioelectrochemistry* **2008,** *72,* 174-182.
(10) Szot, K.; Nogala, W.; Niedziolka-Joensson, J.; Joensson-Niedziolka, M.; Marken, F.; Rogalski, J.; Kirchner, C. N.; Wittstock, G.; Opallo, M. *Electrochimica Acta* **2009,** *54,* 4620-4625.
(11) Nogala, W.; Celebanska, A.; Wittstock, G.; Opallo, M. *Fuel Cells* **2010,** *10,* 1157-1163.
(12) Nogala, W.; Szot, K.; Burchardt, M.; Joensson-Niedziolka, M.; Rogalski, J.; Wittstock, G.; Opallo, M. *Bioelectrochemistry* **2010,** *79,* 101-107.
(13) Schmachtel, S.; Pust, S. E.; Kontturi, K.; Forsen, O.; Wittstock, G. *Journal of Applied Electrochemistry* **2010,** *40,* 581-592.