Preparation and Electrochemical Performance of MnO_x-M/AC (M= La, Ce, Co, Ni) Composites as Oxygen Reduction Catalyst Used in Zinc-air Battery

PAN Lin-mao, NAN Jun-min, SHU Dong, SONG Yan
(School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China)

Abstract: Oxygen reduction catalyst of MnO_x/AC doped with La, Ce, Co, Ni were prepared with thermal decomposition method, and their characteristic and electrochemical performance were investigated by XRD and linear polarization method. Results show that MnO_x/AC doped with appropriate amount of La, Ce, Co and Ni respectively could improve catalytic activity towards oxygen reduction, and those doped with La and Co are slightly more active than the others. The discharge voltages of the simulative zinc-air batteries fabricated with MnO_x-M/AC (M= La, Co) are 1.1236 V and 1.1246 V respectively under the discharge current of 50 mA/cm².

Key words: oxygen reduction catalyst; MnO_x/AC composite; cathodic linear polarization method
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Zinc-air batteries have been a major cause of concern in recent years due to their advantages such as non-polluting, high power, flat discharge voltage and high performance to price ratio[1-2]. Catalytic activity of catalyst in oxygen reduction electrode (ORE) determines performance of the batteries. Manganese oxides[3-4] are promising highly effective catalyst with low cost. Here, active carbon supported manganese oxide composites was prepared as oxygen reduction catalyst by thermal decomposition method, and the effect of doping La, Ce, Co, Ni element on catalytic performance was studied.

1 Experiments

1.1 Preparation of MnO_x/AC and MnO_x-M/AC

MnO_x/AC were prepared by calcined mixture of $Mn(NO_3)_2$ and active carbon (AC). Doped composites MnO_x-M/AC (M= La, Ce, Co, Ni) were prepared following the same procedure by adding other metal (La, Ce, Co, Ni) nitrate. The phase composition of resultants was checked by XRD (Y-2000, China) with CuK_α radiation, 30 kV, 20 mA, and 0.06°/sec.

1.2 Preparation and testing of ORE

Oxygen reduction electrodes with three-layer structure were prepared by a reported method[5]. Thickness of catalyst layer, gas-diffusion layer and final electrode were 0.25, 0.35 and 0.6 mm, respectively.

Linear polarization test was carried out on M6eX (ZAHNER Elektrik, Germany) with a three-electrode electrolytic cell system. Hg/HgO (30% KOH) electrode as reference electrode, ORE with an apparent area of 0.785 cm² as working electrode, and large area nickel plate as counter electrode. Better samples were selected to make simulative zinc-air cell used zinc as anode. Constant current discharge was tested on charge-discharge instrument (Land, Wuhan) controlled by computer.

2 Results and Discussion

2.1 Polarization performance of MnO_x/AC electrodes

As XRD patterns shown in Fig. 1, there are visible peaks in $2\theta = 18°$, 29°, 32°, 36° and 60°, showing that the pyrolytic product mainly belong to tetragonal Mn_3O_4 (JCPDS 24-0734).

At the content range of 6% ~10%, the polarization performance of the electrode enhances as the MnO_x content increase. Only at relatively negative polarization potential area (−0.45 ~−0.7 V), their performance differ from each other obviously. The optimal MnO_x content is 10%.

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作者简介: 潘林茂 (1980年生), 男, 研究生; 通讯联系人: 南俊民; E-mail: jmnan@scnu.edu.cn

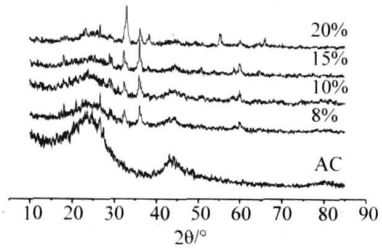

Fig. 1 XRD patterns of as-prepared MnO_x/AC

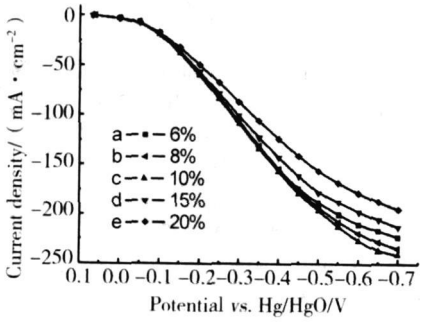

Fig. 2 Polarization curves of MnO_x/AC electrodes

2.2 Electrochemical performance of MnO_x-M/AC (M= La, Ce, Co, Ni) electrodes

It could be observed from Fig. 3 that the polarization performance of electrodes after element doping is improved in a different degree. Electrode doped with Co shows the best polarization performance, while those doped with Ce and no doping element show very similar performance. Electrode doped with La shows the highest voltage (1.5027 V) under open-circuit state. Electrode doped with Co shows the highest voltage (1.12465 V) under discharge state while that of La electrode is (1.1236 V).

3 Conclusions

The optimal content of MnO_x was 10%. Doping La, Ce, Co and Ni respectively could improve oxygen reduction performance. Samples doped with La and Co respectively show higher performance. Voltages of the simulative zinc-air batteries prepared with them are 1.1236 V and 1.1246 V respectively under the discharge current of 50 mA/cm².

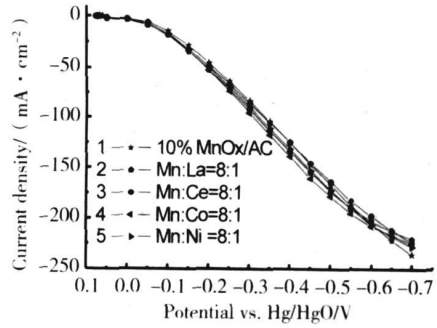

Fig. 3 Polarization curves of MnO_x-M/AC electrodes

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MnO_x-M/AC (M= La, Ce, Co, Ni) 氧还原催化材料的制备及性能

潘林茂, 南俊民, 舒 东, 宋 彦
(华南师范大学 化学与环境学院, 广东 广州 510006)

摘 要: 用热解法制备了掺杂 La, Ce, Co, N等元素的氧还原催化材料 MnO_x/AC, 并采用 XRD和电化学方法对所制备材料的性质和电化学反应性能进行了表征。结果表明, 掺杂适量的 La, Ce, Co和 N等元素可改善电极的氧还原反应性能。掺杂 La和 Co元素的 MnO_x/AC氧催化还原性能最好, 其中, 在 50 mA/cm² 的电流条件下, 使用这两种掺杂材料所制备的模拟锌-空气电池的放电电压分别为 1.1236 V和 1.1246 V。

关键词: 氧还原催化剂; MnO_x/AC; 阴极线性极化
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