The Oxygen Reduction Electrocatalyst Using Pig Blood Pyropolymer As the Precursor

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The proton exchange membrane fuel cell (PEMFC) has good potential applications as the power sources for transportation and stationary applications. However, in order to deliver a long-standing promise of becoming an efficient and commercially viable source of clean energy, the PEMFC need to overcome some formidable technical and economic challenges. One of these challenges is the oxygen reduction cathode catalyst which limits the cost, performance and life-time of PEMFC. Currently, the most effective oxygen reduction reaction (ORR) catalyst is carbon-supported platinum (Pt/C) catalyst. Unfortunately, some critical problems, such as platinum nano-particle agglomeration, detachment and poisoning, have occurred at this catalyst, except for its high cost [1]. Thus, the non-precious metal catalysts (NPMCs) have become the most promising alternative catalyst for oxygen reduction, since Jasinski firstly reported the ORR electrocatalysis of cobalt phthalocyanine in alkaline solution [2]. A large amount of catalytic materials have also been exploited for reducing or replacing the Pt/C catalyst, especially for carbonaceous ORR-active materials. It is indispensable to point out that further research would be also required to promote the ORR activity and their stability, except that they are commonly synthesized by expensive and complex techniques.

In this work, we performed the partial pyrolysis of pig blood below 600℃ under the N_2 atmosphere with a flow rate of 0.5 L/min to form the pyropolymer (PP), which is an intermediate substance between a polymer and carbonaceous material. After doing this, a mixture containing the PP and carbon black (Vulcan XC-72R) has been milled by solid state method for 30 min until obtaining the homogeneous compound as the precursor, and then it was further pyrolyzed in a tube furnace at 700, 800, 900, 1000 and 1100℃ for 2 h under the N_2 atmosphere with a flow rate of 1 L/min. For convenience, based on the PP obtained at 350℃, the catalyst further produced at 900℃ is hereafter called PB350900, and the others are named in a similar manner. Then, the samples were applied on the glass carbon electrode substrate with 5 mm diameter and their electrochemical activity was tested by linear voltammetric method. In addition, some detailed studies were also carried out for obtaining the catalyst with higher ORR activity and better stability, which could compare favorably with the Pt/C catalyst.

Figure 1 showed the ORR activity curves of the catalysts prepared with different pyropolymers obtained from 250 to 600℃ in 0.1 M KOH solution saturated by O_2. All the catalysts have depicted an excellent catalytic behavior in terms of onset potential, cathode peak potential and limited current, but it was undoubted that the characteristics of the PPs have also played an important role in improving the ORR activity. It can be found that the PP formed at 350℃ was more suitable for preparing the ORR catalyst because of its more positive onset potential and large limited current. Moreover, the structure of these catalysts was characterized by X-ray diffraction spectra, as shown in Figure 2. No peaks were observed except for two board peaks including the large broad peak at 2θ = 25° and small broad peak at 2θ = 44°. Those peaks could be attributed to amorphous carbon phase, usually observed for activated carbon [3].

In addition, the ORR curves of the catalysts obtained at different heat-treated temperatures have also been tested. It can be found that the heat-treated temperature had a large effect on ORR catalytic performance of different catalysts with the same pyropolymer. The difference in ORR activity might be ascribed to the formation behavior of ORR-active sites and pore development. Comparing with all the LSV curves, the PB3501000 had the best electrocatalytic activity for ORR with the most positive onset potential of 0.03 V and the largest limited current of 0.233 mA, which could compare to the Pt/C catalyst.

The present work would highlight the development of a novel cathode ORR catalyst using inexpensive and widely available pig blood pyroploymer as the precursor. Optimization of the carbon black activation and pyrolysis process will be further discussed, with the impact on surface structures and pore volumes and the ORR mechanism will be also intensive explanation.

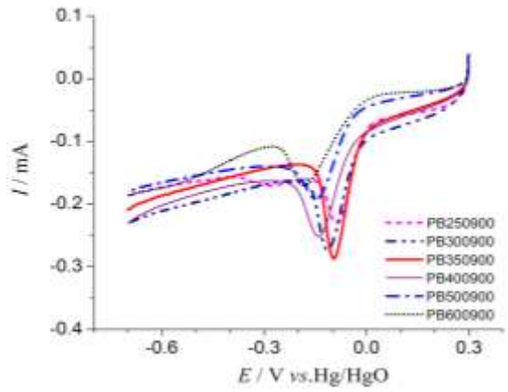

Figure 1: LSV curves of the catalysts prepared with different pyropolymers recorded in O_2-saturated 0.1 M KOH solution at 5 mV/s.

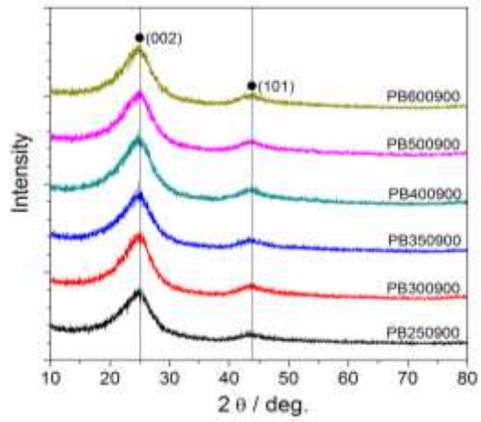

Figure 2: XRD patterns of the catalysts prepared with different pyropolymers.

Acknowlegements
This research was supported by Natural Science Fund of China (Project No.21273292) and the Fundamental Research Funds for the Central Universities (Project No. CDJXS12220002).

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