The oxygen reduction reaction catalyzed by carbon-supported copper phthalocyanine tetrasulfonic acid (CuPcTSA/C) by high temperature treatment

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The oxygen reduction reaction (ORR), which dominates the overall electrochemical processes in both fuel cells and metal-air batteries, has drawn great effort in order to improve its catalytic reaction kinetics. Pt has been known to be the best catalyst for the ORR due to its high catalytic activity. However, the high cost and insufficient electrochemical durability of Pt-based catalysts still blocks the better commercialization of fuel cell tecnhology[1-3]. Up to date, the current important issue is to look for new non-precious metal alternative catalysts to replace Pt.

Phthalocyanine and its transition metal derivatives have become the hot spot due to their unique metal-N4 macrocycle structural performance. Among them Fe- and Co-centered MPc complexes are validated for the most promising non-noble metal catalysts[4-6]. Recent studies suggest that other metal-centered phthalocyanine such as CuPc/C also can be a novel catalyst for the ORR[6-7]. The hydrophilic phthalocyanines, especially sulfonated derivatives, have attracted much attention as a potential material. Based on this conception, in this work, the carbon-supported copper phthalocyanine tetrasulfonic acid (CuPcTSA/C) was chosen to be as the cathode catalyst for the ORR and its electrocatalytic activity was investigated in alkaline electrolyte.

CuPcTSA/C catalysts were prepared by combining a mixture of 40 mg CuPcTSA and 60 mg carbon black in a mortar, milling by adding 10 ml methanol for 2h, then was vacuum-dried at 40^{o}C for 1h to remove methanol. The resulting powders were placed in a quartz boat and pyrolyzed at 600, 700 and 800^{o}C for 120 min at a rate of 20 ^{o}Cmin^{-1} in a flowing nitrogen atmosphere. The kinetics and electrocatalytic activity on the CuPcTSA/C catalyst have been measured using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and rotating disk electrode (RDE) technique.

Figure 1 displays the CVs of CuPcTSA/C catalysts without heat-treatment and heat-treated at 600^{o}C, 700^{o}C and 800^{o}C, respectively. As shown in Fig. 1, the peak potential of oxygen reduction increased from 0.02 V for CuPcTSA/C without heat-treatment and increased to -0.08 V for CuPcTSA/C treated at 700^{o}C, and then decreased when the treating-temperature was further increased to 800^{o}C. The current density has the same trend along with the half-wave potential, ie., both go up from 600^{o}C to 700^{o}C and turns to go down with additional increasing the temperature to 800^{o}C.

Figure 2 shows the polarization curves of the CuPcTSA/C before and after heat treatment in O_2-saturated 0.1 M KOH at room temperature. One can see that CuPcTSA/C without heat-treatment showed a half-wave potential at -0.18. The electrocatalytic activity catalyst is clearly improved with the increasing temperature from 600^{o}C to 700^{o}C, where the half-wave potential was positively shifted by about 160 mV~180 mV. However, with the temperature turning up to 800^{o}C, the activity falls, the half-wave potential of 600^{o}C and 800^{o}C are at -0.02 and -0.01, respectively, and both are lower than that of 700^{o}C.

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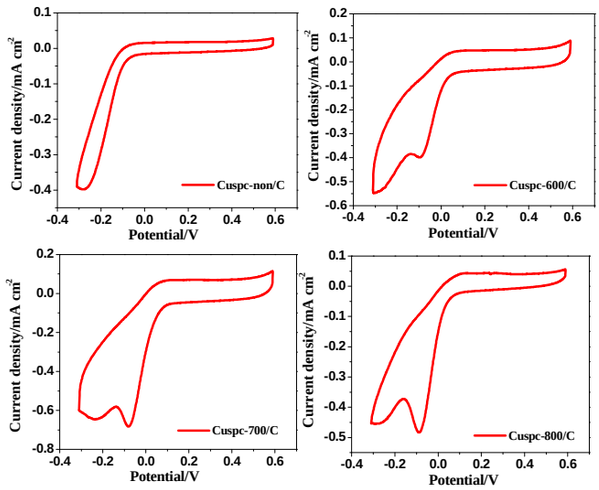

Figure 1: Cyclic voltammograms of CusPc/C catalysts without and 600 ^{o}C, 700^{o}C, 800^{o}C heat-treated Solution: 0.1M KOH; Scan rate: 50mV s^{-1}

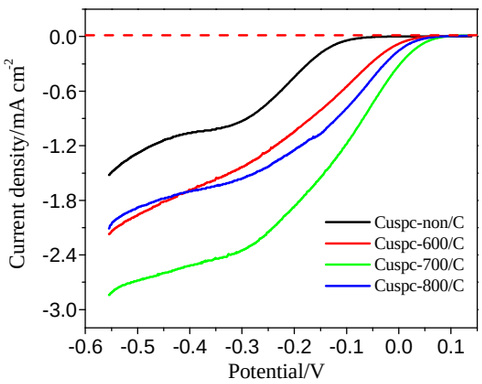

Figure 2: Polarization curves of the CusPc/C catalysts with different heat treatment temperature in an oxygen-saturated 0.1mol·L^{-1} KOH solution. Scan rate: 5mV/s. Electrode rotation rate: 1500rpm.