A possible way of improving the catalytic activity of heat-treated non-precious Metal-N4 Macrocycles for the reduction of O_2

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The ever expanding worldwide energy needs have made fuel-cells an important and permanent topic of research. However, their massive application in daily life has been hampered in part by the high cost of catalytic materials for the O_2 cathode that usually uses noble metals like Pt. In volcano correlations where the catalytic activity is plotted versus the energy biding of O₂ to different metals Pt is located at near the apex of the volcano, so much improvement of the activity of Pt-catalytic Most materials cannot be achieved. improvements are achieved by reducing the Pt loading and by decreasing the size of particles of Pt containing materials and alloys. On the other hand, metallophthalocyanines and metalloporphyrins are well known as electrocatalysts for the reduction of O_2 (ORR) and have been extensively investigated (1), together with other similar molecules as "nonprecious metal catalysts" with the aim of replacing Pt in fuel cells (2). In such N4 chelates, molecular oxygen binds reversibly but they lack long-term stability in the aggressive environment of a fuel cell and new heat-treated materials have been developed to overcome this problem. Many papers have been published (2-5) where they demonstrate that heating MN4 metal macrocyclics together with carbonaceous materials and conducting polymers at temperatures as high as 1000 °C produce materials of ill-defined structure. There is much controversy about the nature of the active site and the structure that surround the metal center. It is also not clear why the treated materials exhibit such high catalytic activities approaching those of Pt containing catalysts. In many papers (1) our group has demonstrated that the catalytic activity is directly linked to the M(III)/(II) formal potential, the more positive the highest the activity (1). For example for Fe-containing MN4 catalysts a plot of log k gives a straight line with a slope of +0.160 V/decade, i.e. giving a slope that is close to a Tafel slope of -0.120 V/decade but with opposite sign. This shows that the activity

follows a Tafel-like correlation with the formal potential (see Figure 1). Recently, we have propes that of the very high activities of the heat-treated CNxM materials (x=2,4) con be explained by the shift of the formal potential of the MN4 moiety to more positive values, but fortmal potentialsof these materials all well belor the reduction potential of Pt oxides (see Figure 1, right) which is close to 0.8 V.

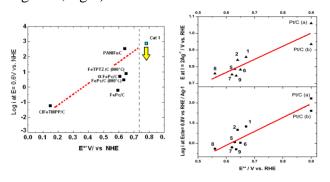


Figure 1. Correlations of activity the M(III)/(II) formal potential of the pyrolyzed and non-pyrolyzed MN4 catalysts compared to Pt/C. Adapted for ref. (5)

Our studies suggest that preparing prepare heattreated materials that would have redox couples more shifted to more extreme positive potentials (ca 0.8 V) using electron-acceptor species around the metal that could survive the high pyrolyzing temperatures. Catalysts heat-treated at 1000°C do not exhibit clear redox couples but this is the right direction to go and hypothetically overpass the catalytic activity of Pt. Hopefully a volcano correlation is not found so to go beyond 0.8 V. This paper shows that there is a clear hope of obtaining catalysts better than Pt and having cheaper fuel-cells for broad applications. Some other explanations of these trends will be discussed that propose a new semi-empirical model of electrocatalysis.

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