

SYNTHESIS OF ELECTROCATALYSTS FOR O₂ REDUCTION CONTAINING COBALT, NITROGEN AND CARBON

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Oxygen reduction in gas diffusion electrodes attracts considerable interest primarily because of its impact on various energy-related fields, such as fuel cells and metal-air batteries. As an electrocatalyst for this reaction, platinum has traditionally been employed (1) but, due to its high cost, less expensive potential alternatives are being actively searched for. Among these, carbon-supported metal macrocycles exhibit very good activity (2) and stability and are currently employed in mechanically recharged metal-air batteries for electrical traction (3).

In pyrolyzed metal macrocycles the molecular structure of the catalyst is destroyed during the heat treatment so that the metal complex is in fact only a precursor of the actual active material (4). It is thus appealing to try to reproduce these electrocatalysts starting with different precursors of lower cost and easier availability, and to disclose the reasons for their activity so as to be able to improve their performance.

In a previous work (5) we have shown that if Cobalt tetramethoxyphenylporphyrine (CoTMPP) is pyrolyzed at 900°C with carbon black a very active electrocatalyst results for O₂ reduction in gas diffusion electrodes. Analysis of the composition of the pyrolyzed material showed that some Co₃O₄ was present. For this reason, the activity of Co₃O₄ synthesized from different precursors was investigated. Co₃O₄ from CoCO₃-impregnated carbon black was found to be the most active catalyst. Nevertheless its activity was lower than that of pyrolyzed CoTMPP. Reasons for replacing the latter catalyst are twofold: (i) its precursor is expensive and troublesome to synthesize, and (ii) it is intriguing to find out the origin of its activity.

We have carried out a systematic study of composite materials containing all the ingredients of CoTMPP, *i.e.*, cobalt, nitrogen and carbon, but put together from different precursors in different conditions. Electrocatalysts were first synthesized from two different mixtures of precursors:

- (a) CoCO₃ + TMPP, pyrolysis in air at 200-800°C, mechanical mixture with C;
- (b) Co₃O₄ (from CoCO₃) + TMPP, pyrolysis in air at 200-800°C, mechanical mixture with C.

Fig. 1 shows that type (a) electrocatalysts are always less active than pyrolyzed CoTMPP. The activity decreases with increasing calcination temperature. The same is the case for type (b) electrocatalysts type. The results indicate that the presence of carbon during pyrolysis is essential to achieve high electrocatalytic activity.

Next step was to synthesize electrocatalysts from composite precursors containing carbon + CoCO₃ + TMPP. Carbon was impregnated with the other precursors, then pyrolyzed in inert atmosphere. Fig. 2 shows dramatic differences in the voltammetric curves. In particular, the voltammetric charge is orders of magnitude higher for the composite electrocatalysts than for pyrolyzed CoTMPP. Fig. 3 shows that also the activity

for O₂ reduction is definitely higher for the synthetic electrocatalysts.

Work is in progress to optimize all the parameters of the system.

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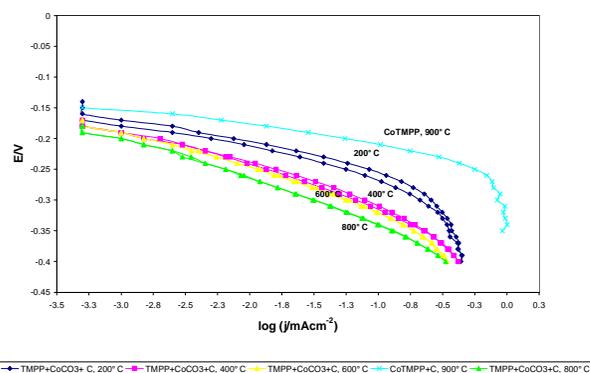


Fig. 1 - Polarization curves in O₂-saturated alkaline solution of CoCO₃ + TMPP pyrolyzed at various temperatures, then mixed with carbon.

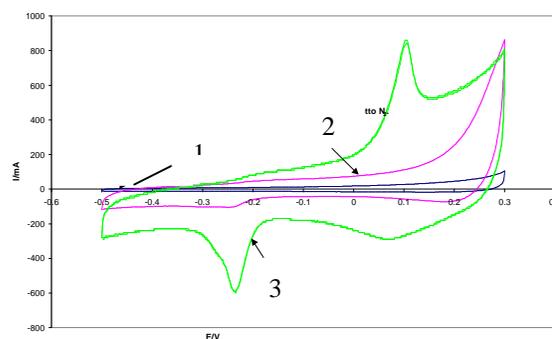


Fig. 2 - Cyclic voltammetry in N₂-saturated alkaline solution. 1) CoTMPP pyrolyzed at 900°C; 2) CoCO₃ + TMPP + C at 400°C; 3) Same as 2 but at 800°C.

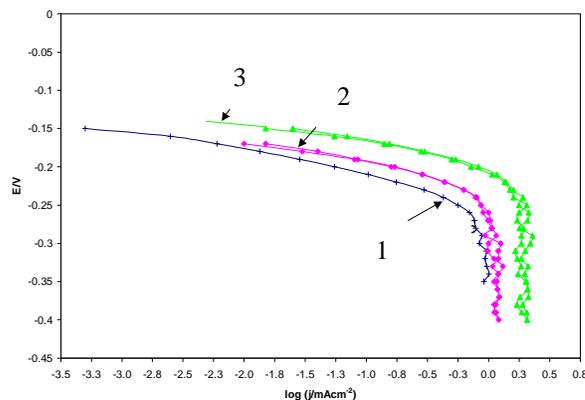


Fig. 3 - Polarization curves in O₂-saturated alkaline solution. 1 to 3 as in Fig. 2.

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