

NON-NOBLE ELECTROCATALYSTS FOR ALKALINE FUEL CELLS

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Summary

Doping of solid phase precursors, followed by pyrolysis or co-pyrolysis of gas-phase precursors, has resulted in catalysts suitable for oxygen reduction in alkaline fuel cells.

Introduction

Noble metals, when used as electrocatalysts for oxygen reduction in metal-air batteries and fuel cells, suffer from the disadvantages of high cost, susceptibility to poisoning, and sintering. Carbons activated with macrocyclics have attracted increasing attention as alternative electrocatalysts for oxygen reduction [1]. The initial activity of these catalysts is good, but performance declines rapidly. Pyrolyzing the macrocyclic on the carbon support leads to enhanced stability and the catalyst retains good activity [2]. The exact nature of the catalytic sites after pyrolysis is still under investigation [3, 4].

Despite this promising method of treating macrocyclic activated carbon catalysts, the performance decay is still too large to be acceptable. Part of the stability problem occurs because the catalytic layer on the carbon surface is, at most, a few monolayers thick. The approach described here is designed to develop bulk doped catalysts with similar structures to pyrolyzed macrocyclic catalysts. The transition metal and coordinated ligands are dispersed throughout the bulk of the conductive carbon skeleton.

Two approaches to realizing this concept are being pursued, both involving the doping of a carbon precursor followed by high temperature pyrolysis to form an M-N-C catalyst. In one approach, the precursor is a solid phase ion exchange resin. Two resins have been selected for doping. One is IRC-50 (Rohmond Haas) (Fig. 1(a)), which is a weak cation exchange resin that contains no nitrogen in its backbone or exchange groups. The transition metal and nitrogen are introduced by either exchanging a transition-metal (such as Fe^{3+} from FeCl_3) and nitrogen (from NH_4OH) sequentially or exchanging a chelation compound (such as $\text{Fe}(\text{bipy})_3^{2+}$). The other ion ex-

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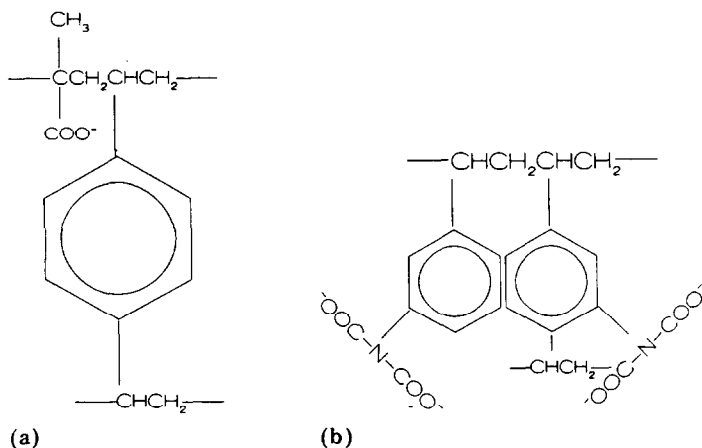


Fig. 1.(a) Structure of IRC-50 weak acid ion exchange resin; (b) structure of Chelite-C.

change resin chosen was Chelite-C (Fig. 1(b)) which contains a nitrogen-containing iminodiacetic acid exchange group. Exchange of a simple transition metal salt results in metal-nitrogen coordination before pyrolysis.

In the second approach, gas phase precursors are mixed in a reactor and pyrolyzed to form the catalyst. Acetylene (C₂H₂) is used as the carbon source, ammonia (NH₃) as the nitrogen source, and an iron-containing organometallic as the transition metal source.

Experimental

Chelation compounds for doping the IRC-50 resin have included Fe(bipy)₃SO₄, Co(bipy)₃Cl₂, Fe(phen)₃SO₄, Co(NH₃)₆Cl₂, and Co(en)₃Cl₃. Doping is carried out by mixing the resin with a solution of the dopant and agitating the mixture at 80 °C for 3 h. The doped resin is dried and then placed in a tube furnace. The resin is pyrolyzed under an NH₃ atmosphere at temperatures near 900 °C.

The gas phase precursors are pyrolyzed in a vertical tube furnace at temperatures near 1100 °C. The C₂H₂, NH₃, and iron-containing organometallic are introduced at the top of the furnace. Product is collected in a water trap at the bottom of the furnace or inside the tube.

Electrodes are prepared from the bulk doped carbons by mixing the catalyst with PTFE and spreading onto an Ag-plated Ni screen.

Electrochemical tests are performed using the floating electrode technique [5]. The electrolyte is 30% KOH and the temperature is held at 80 °C. The electrodes are tested galvanostatically and the measurements are corrected for external ohmic losses. Potentials are reported *versus* a dynamic hydrogen electrode (DHE).

The catalysts are analyzed for their carbon, hydrogen, nitrogen, and metal content. Some catalysts have also had BET surface areas determined using a Micromeritics Flowsorb II surface area analyzer.

Mössbauer spectroscopy has been used in an attempt to identify the species present in the iron-containing catalysts. This work is being done in conjunction with Professor Daniel Scherson at Case Western Reserve University.

Results and discussion

Electrochemical tests

Figure 2 compares the electrochemical performance of catalysts prepared from IRC-50 doped from solutions of $\text{Fe}(\text{bipy})_3\text{SO}_4$, $\text{Co}(\text{en})_3\text{Cl}_3$, $\text{Co}(\text{bipy})_3\text{SO}_4$, $\text{Co}(\text{NH}_3)_6\text{Cl}$, and $\text{FeCl}_3\text{-NH}_4\text{OH}$ with CoTMPP adsorbed and pyrolyzed on Vulcan XC-72. There is a large improvement in performance on changing the dopant solution from $\text{FeCl}_3\text{-NH}_4\text{OH}$ to $\text{Fe}(\text{bipy})_3\text{SO}_4$ with the same resin and pyrolysis conditions. The $\text{Fe}(\text{bipy})$, $\text{Co}(\text{en})$, and $\text{Co}(\text{hex})$ systems show a performance that is 50 - 80 mV less at 100 mA cm^{-2} than the CoTMPP on Vulcan XC-72. The surface areas of $\text{Co}(\text{en})$, $\text{Co}(\text{hex})$ and $\text{Fe}(\text{bipy})$ doped carbons are in the same range as CoTMPP doped Vulcan XC-72. The differences in the kinetic region may be attributed to the differences in the surface concentrations of the catalyst.

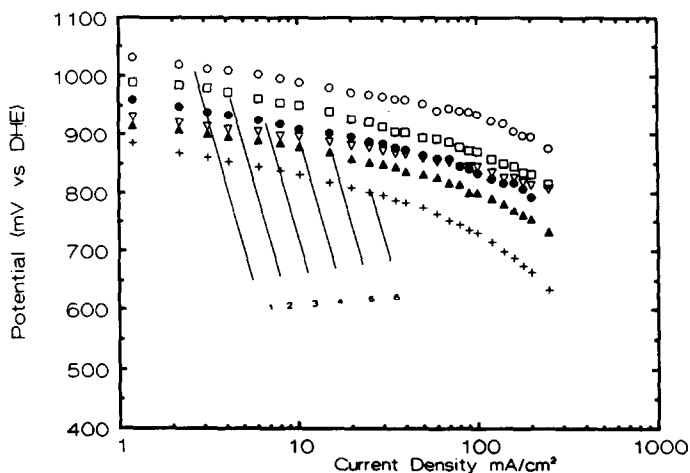


Fig. 2. Polarization curves for O_2 reduction with porous electrodes in 7 M KOH at 80°C .

- 1, 4.8% w/w Co-TMPP on XC-72 carbon;
- 2, IRC-50 + Fe (added as bipyridyl complex);
- 3, IRC-50 + Co (added as the hexamine chloride);
- 4, IRC-50 + Co (added as tris ethylenediamine cobalt(III) chloride);
- 5, IRC-50 + Co (added as bipyridyl complex);
- 6, IRC-50 + Fe (added as the chloride) + N (added as NH_4OH).

The earlier drop-off of performance may be due to either ohmic losses in the structure or hindrance to oxygen transport. The Co(bipy) system shows somewhat poorer performance; stoichiometric analysis of the Co(bipy) system showed that only 1% Co was incorporated in the final catalyst (compared with 10% for iron) and, therefore, doping conditions need to be adjusted.

The next set of experiments examines two different approaches for the synthesis of "Fe-N" complexes. Figure 3 compares the performance of the IRC-50 Fe(bipy) system with Chelate-C doped with FeCl₃. In the first system, the Fe is already coordinated with nitrogen in the bipyridine complex. Introducing this complex into the ion exchange resin allows bulk-doping, and ensures molecular level interaction between the carbon and the "Fe-N" complex. In the second system, the resin has a backbone that contains nitrogen and coordinates with the iron. In addition to differences in the density of the exchange sites (which determines the metal/nitrogen ratio) in these two systems, the molecular interactions are bound to be different, which may result in differences in oxygen reduction performance. The carbon prepared from the chelating resin shows essentially the same performance in the kinetic region, indicating that the nature of the Fe-N complexes may be similar, regardless of their method of preparation as long as covalent type interactions are ensured as opposed to purely ionic type interactions. At higher current densities, there are some differences in the performance of these systems, which may be attributed to the non-optimized electrode preparation. It is also quite possible that the stabilities of these complexes may vary widely. Preliminary examination of the catalysts using Mössbauer spectroscopy indicates that the IRC-50 and Chelate-C

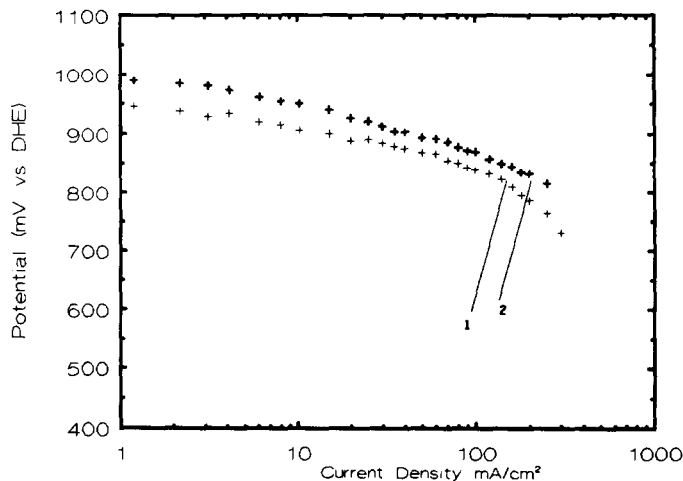


Fig. 3. Polarization curves for O₂ reduction with porous electrodes in 7 M KOH at 80 °C. 1, Chelate-C + Fe (added as the chloride), pyrolyzed at 900 °C; 2, IRC-50 + Fe (added as the bipyridyl complex), pyrolyzed at 900 °C.

systems contain one species in common and one species each that is unique to that catalyst.

Figure 4 shows the results of performance measurements on catalysts from gas phase precursors. The undoped carbon prepared from gas pyrolysis shows very poor performance. Addition of the Fe and N has a dramatic effect on performance. The surface area of the Fe/N doped carbon in this Figure is only $19 \text{ m}^2 \text{ g}^{-1}$ and the nitrogen/metal mole ratio is 0.46. Studies are in progress to improve both these factors.

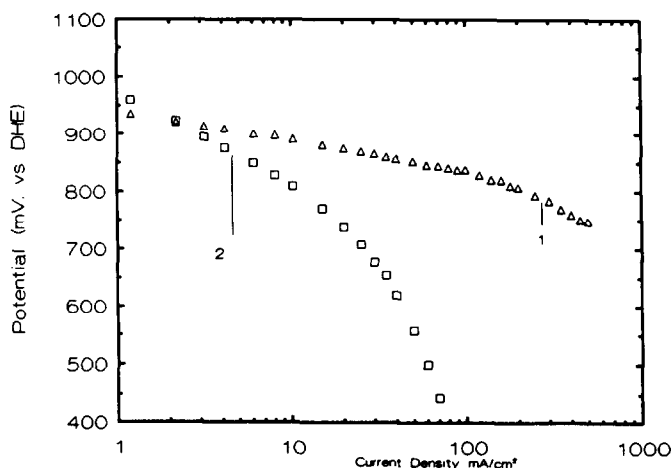


Fig. 4. Polarization curves for O_2 reduction with porous electrodes in 7 M KOH at 80°C . 1, Electrode was made with pyrolyzed $\text{C}_2\text{H}_2 + \text{Fe}$ (added as dimethylaminoethylferrocene); 2, pyrolyzed C_2H_2 (1000°C).

Characterization of catalysts

The catalysts are routinely analyzed for carbon, hydrogen, nitrogen, and metal contents. Table 1 shows the stoichiometry calculated for some typical catalysts. There is still some unknown that is not accounted for in the C, H, N, M. Some of this unknown is oxygen which comes from the COO^- groups in the resin and exposure of catalyst to the atmosphere. The oxygen is present in the form of metal oxides. However, a calculation of the maximum weight percentage of oxygen present in this form shows that it is not enough to account for all of the unknown. The sample of IRC/Fe-(bipy) was also sent for Si determination. Some Si is present, but Si or SiO_2 does not account for all of the unknown. Emission spectroscopy was used to determine if any other heavy metals were present. Only minor amounts were present. The sample was sent for sulfur determination which showed that some sulfur was present. This sulfur is probably from the sulfate group in the $\text{Fe}(\text{bipy})_3\text{SO}_4$. This is because some of the dopant is imbibed in the pores of the IRC-50 instead of being ionically bound to the COO^- groups.

BET surface areas of catalysts prepared from the doped ion-exchange resin precursors are in the range $100 - 300 \text{ m}^2 \text{ g}^{-1}$. When the IRC-50 resin

TABLE 1

Catalyst	Wt.%					Surface area (m ² g ⁻¹)
	C	H	N	M	Unk	
IRC 50/Fe(bipy)	70.70	0.75	2.36	9.60	16.59	210.5
IRC 50/Co(bipy)	85.86	0.19	0.210	1.18	12.56	87.3
IRC 50/Co(en)	88.42	0.31	0.620	10.8	0	150.4
IRC 50/Co(hex)	96.28	0.29	0.10	2.63	0.7	205.3
Chelite-C/Fe	79.6	0.22	0.190	13.5	6.4	191.1
Gas phase carbon	99.00	0.5	—	—	0.5	
Gas phase/ferrocene derivative	78.34	0.34	1.38	12.00	7.90	19

with no dopant was pyrolyzed, the surface area was less than 5 m² g⁻¹. This is consistent with work in progress which indicates that the presence of the metal dopant has a large effect on the nature of the pyrolysis process.

Conclusions

The doping of solid phase precursors, followed by pyrolysis or the copyrolysis of gas phase precursors, has allowed us to produce catalysts with good activity toward oxygen reduction. Efforts are currently underway to understand better the reasons for the catalytic activity of the bulk doped catalysts with a view to further improving their activity.

Acknowledgement

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