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AUTHOR(S) Nicholas E. Vanderborgh and Peter C. Rieke

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 **Los Alamos** Los Alamos National Laboratory
Los Alamos, New Mexico 87545

PYROLYZED MACROCYCLE/CARBON BLENDS FOR ADVANCED ELECTROCATALYSTS

Nicholas E. Venderborgh and Peter C. Rieke
Los Alamos National Laboratory
Electronics Division, Los Alamos N.M. 97545 USA

INTRODUCTION

Hydrogen-air acid fuel cells suitable to power various stationary or mobile devices are readily powered by liquid methanol following a reforming step. Anticipated applications dictate high current densities, 150 mA/cm² or higher, and thus porous carbon electrodes have incorporated metallic electrocatalysts that include platinum or other metals. During the past years several groups have shown that certain pyrolyzed macrocycle/carbon blends produce active surfaces for oxygen reduction.(1-3) These results point to the eventual elimination of precious metals from fuel cell electrodes and could significantly lower the cost of energy conversion devices.

These electrocatalysts are prepared by pyrolysis of dry blended mixtures of carbon blacks and metal ion containing organic chelates, typified by phthalocyanines or porphyrins containing one of the transition elements, e.g., iron or cobalt.(3) Pyrolysis at 500 to 850°C forms a char which is then formulated into a porous electrode structure for oxygen reduction. Results suggest reduction activity that exceeds metallic platinum, at least at lower current densities.(3)

The electroreduction of molecular oxygen at carbon surfaces or supported metal surfaces has received extensive study, driven by the technical importance of various fuel-air conversion devices. Although the details of many molecular steps are still not defined, it is now apparent that electroreduction follows a pathway shown in Figure 1. Dioxygen, in the most stable triplet state(4), adsorbs onto a surface site, perhaps preferentially within certain sized pores.(5) There the first electron, and perhaps, a proton, is added to the molecular adduct to form the superoxide ion. Most likely this first one electron addition contributes to the slow kinetics of the oxygen reduction step.(4) The actual degree of protonation is not clear for, although the pK_a values of various molecular intermediates are known(4), the surface acidity is not well understood. Addition of the second electron forms HO₂, which may desorb to form a stable product, or dissociate to form molecular water and another oxygen radical. This partition depends upon relative rates of k₂ and k₃. Finally, additional electron and proton donation occur to form sorbed water that migrates to regenerate the site. This figure illustrates the sequential nature of electron addition and the desorption of unreacted hydrogen peroxide to form a two electron product. In this reduction scheme, the electrocatalysis must participate in several unique processes: oxygen adsorption, electron transport from a conductive zone, hydrogen peroxide decomposition (for the four electron process) and ionic (probably protonic) transport. Lastly, the active site must be promptly regenerated. It is within this concept that the performance of these pyrolyzed blends must be understood (6)

PYROLYSIS STUDIES

The emphasis of these studies has been compounds with a metallated N₄ center, especially phenyl porphyrins. Previous work explored the fate of this molecular array since this chelate is thought effective in π overlap with oxygen orbitals.(2) Chemical analysis suggests that the metal to nitrogen ratio in the char are similar to the starting material. However microscopic examination of the char shows residual metals tend to cluster in spheruloids while spectroscopic studies question the maintenance of the N₄ chelate (1,3)

Studies reported here monitor the pyrolysis process, both with metal free and metallated porphyrins and with porphyrin/carbon blends. Figure 2 shows thermogravimetric data for Ni(II) tetraphenylporphyrin (Ni TPP) and shows the effect of heating rate upon the pyrolysis reaction. Samples were maintained in a flowing Ar 6% H₂ stream that included a fixed quantity of H₂O (18 mm Hg). Appreciable weight loss began when a temperature of 425°C was reached. Then, a constant weight was observed as heating was continued between 550 and 650°C. At higher temperatures weight is again lost at relatively constant rates, independent of temperature, until finally a stable residual char results. Data in Figure 2 show programmed heating to 850°C

and then an isothermal measurement at that temperature. At lower heating rates larger quantities of material are lost during the first, low temperature step and a smaller residual quantity is observed. At the higher rates, the first process results in less weight loss and the final product mass formed during the 850°C isothermal step is larger.

The first weight loss represents sublimation, for unaltered material can be recovered from cooler parts of the furnace and exhaust system. Exhaust through the crucible cover vent is slow and the quantity lost depends upon the temperature profile. At higher heating rates the product is retained in the heated zone where pyrolysis occurs. This degradation results in a web like deposit that fills the crucible volume with a highly porous material. Observation of this by interruption of a thermal cycle shows that this solid slowly disappears during the high temperature processing. The final char is conductive and has uninformative infra red spectra and appreciable metal content. At 850°C, less than 10% of the original mass is retained.

Data were also determined for Ni TPP in pyrolysis environments with different oxygen partial pressures. In these studies thermal environments were altered by controlling the hydrogen to steam ratio in the purge gas. As can be seen in Figure 3, the first sublimation process is unaffected by the oxygen partial pressure. However, increasing oxygen partial pressure alters the final char weight and the thermal stability of the material. Thus the temperature, the heating rate and the nature of the gaseous environment are all important factors in determining the residual product.

Many studies have explored alteration of carbon blacks following thermal treatment. Data on three candidate carbons, shown in Figure 4, include the temperature where weight loss first became appreciable and then the normalized rate of weight loss during a 950°C isothermal step, in an Ar 6% H₂ mixture. As shown, the initial pyrolysis temperature depends upon carbon type, but the weight loss rates during the isothermal portion of the trace are similar.

Experiments were conducted on mixtures of both treated and untreated carbons and metallated porphyrins. In a typical experiment, for example, a carbon black (Cabot XC 72) was mixed with Co TPP (19.1% Co TPP) and then this mixture was heat treated in Ar 6% H₂. No weight loss was apparent until temperatures of 490°C were reached and then a weight loss occurred between 600 and 850°C with a rate independent of temperature. On the basis of demonstrated thermal behavior of the two separate components, we predict a total weight loss of 20.7% at 800°C; in fact less than half of this was observed (9.4%). Microscopic examination of the carbon showed that the product carbon surfaces were altered by the deposition of small (10 Å) spherical particles firmly bound to the carbons. This surface deposit is only apparent when the mixture is pyrolyzed.

CONCLUSIONS

Pyrolysis of metallated macrocycle compounds involves a vapor phase condensation to form a solid, condensation product that is carbonaceous and electrochemically conductive. Reaction of these vapors with hot carbon surfaces permits condensation on these surfaces that prepares active electrocatalytic carbons. The role of the metal ion in these processes is not clear, although the chelate clearly acts to carry the metal into the vapor phase. Rapid peroxide decomposition results only with the composite (carbon plus chelate) char. Thus these modified surfaces add the necessary peroxide reactivity to carbon for high oxygen electroreduction rates.

ACKNOWLEDGMENT

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REFERENCES

1. D.A. Scherson, et al., *Electrochimica Acta* 28, 1425 (1983).
2. K. Vizenor, *Elektrokhimiya*, 18, 758 (1982).
3. J.A.S. Holt, et al., "Investigation of Alloy Catalysts and Redox Catalysts for Phosphoric Acid Electrochemical Systems, Report FC-717/E, International Fuel Cells, South Windsor, CT, October 1985.
4. H.S. Prago, *The Coordination Chemistry of Metalloenzymes*, D. Reidel Publishing Company, p. 247 (1981).
5. K. Kinoshita and J.A.S. Holt, *Carbon*, 11, 237 (1981).
6. A. Matsumura, et al., *New Materials and New Processes*, 2, JEC Press, Inc., 85 (1981).

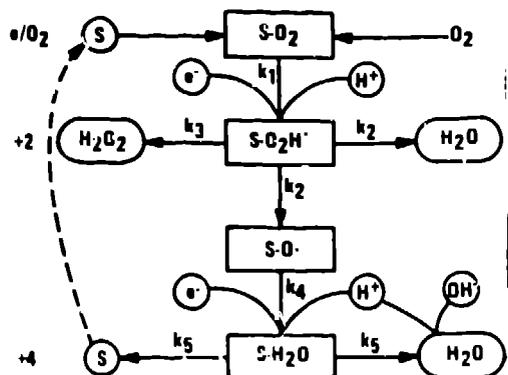


Figure 1: Mechanistic Pathway for Electrochemical Reduction of Dioxygen: Molecular oxygen reacts with a surface site (S) and then one electron is added to form the superoxide ion; following that kinetically slow step, hydrogen peroxide is formed which decomposes to form product water and another surface oxide. Acidity at surface dictates protonation rates. Less probable two-site absorption is not shown.

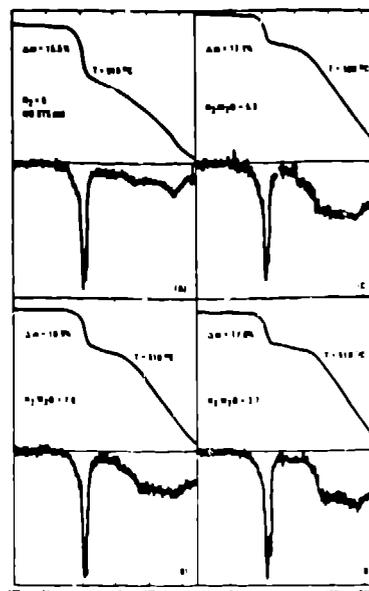


Figure 3: Effect of the Gaseous Environment on Pyrolysis of Ni-TPP: Data show pyrolysis with different H_2/H_2O ratios, all at 5 K/min. Weight loss is for initial, low temperature process while the temperature indicated is that of maximum weight loss. Bottom trace shows the dm/dT behavior.

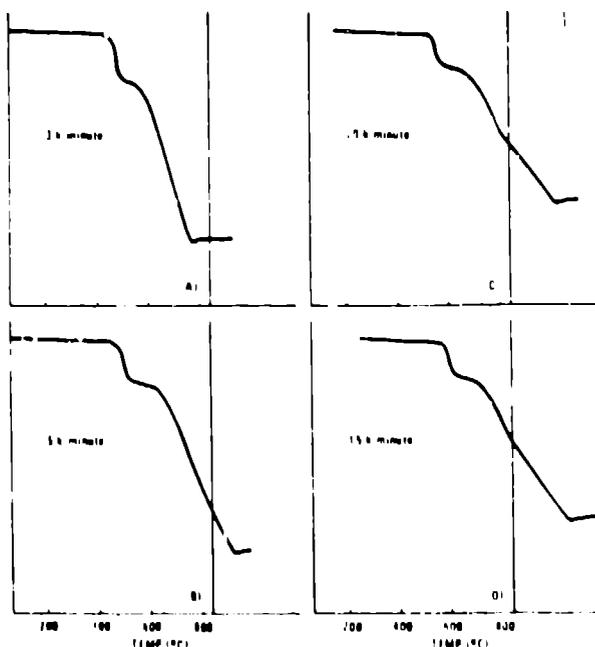


Figure 2: Effect of heating Rate on Ni-TPP Pyrolysis: Data show pyrolysis in an Ar 6% H_2 mixture with water saturated at 100°C (10 mm). Experiment used Al₂O₃ covered crucible heated from 50 to 950°C and then held at 950°C for 10 minutes.



Figure 4: Pyrolysis Behavior of Three Candidate Carbon Blacks: Data show thermal behavior in Ar 6% H_2 heated from 50 to 950°C and then held at 950°C for 10 minutes.