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COOPERATIVE AGREEMENT NUMBER DAMD17-97-2-7011

TITLE: Portable Electrochemical Oxygen Concentrator for Battlefield Combat Casualty Care

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REPORT DATE: March 1998

TYPE OF REPORT: Final

PREPARED FOR: U.S. Army Medical Research and Materiel Command
Fort Detrick, Maryland 21702-5012

DISTRIBUTION STATEMENT: Approved for public release;
distribution unlimited

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
March 1998

3. REPORT TYPE AND DATES COVERED
Final (1 Jul 97 - 28 Feb 98)

4. TITLE AND SUBTITLE
Portable Electrochemical Oxygen Concentrator for Battlefield Combat Casualty Care

5. FUNDING NUMBERS
DAMD17-97-2-7011

6. AUTHOR(S)
Burk, Melvyn

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Freshaire Systems and Technologies, Inc.
Cleveland, Ohio 44122-3853

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Medical Research and Materiel Command
Fort Detrick, Maryland 21702-5012

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The primary goal of this overall research and development program is to design and construct a portable electrochemical oxygen concentrator (PECOC) capable of producing nearly pure (> 98%) oxygen from the ambient atmosphere at room temperature. This novel device relies on the two-electron reduction of oxygen to peroxide at a high area carbon-based, gas-permeable, Teflon-bonded (HAC-GPTB) cathode, which then migrates through a thin solid polymer electrolyte (SPE) membrane to a gas-diffusion (GD) anode, where it is oxidized to yield dioxygen. Two major aspects were emphasized during this first six-month period: the identification of highly active, highly specific electrocatalysts for the two-electron reduction of O_2 to peroxide and for the oxidation of peroxide to O_2 in acid media and the construction of a prototype stack reactor capable of delivering pure oxygen at levels comparable to those required for field medical applications (3 L/min). Significant progress was made in both of these areas. In particular, a simple surface modifier for platinum was found to promote the quantitative reduction of dioxygen peroxide at small overpotentials in dilute phosphoric acid as evidenced by rotating ring-disk techniques results. Furthermore, a full size PECOC unit built from commercially procured materials was shown to deliver pure dioxygen in several independent trials.

14. SUBJECT TERMS
electrocatalysts, oxygen concentrator, electrochemical oxygen generation

15. NUMBER OF PAGES
26

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unlimited

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5. INTRODUCTION

A. BACKGROUND

I. Oxygen for Medical Applications

The beneficial effects of high purity oxygen in the treatment of a variety of ailments, including surgical procedures, is widely recognized by the medical community [1,2]. Pure oxygen, as a compressed gas or a liquid, is readily available throughout the US. However, the large weight-to-volume ratio, high replacement frequency, and safety hazards associated with the handling of pressurized containers make these forms of pure O_2 highly impractical for field and ambulatory applications. An approach that eliminates logistical problems of transport and storage, involves the extraction of O_2 from the ambient atmosphere, either by pressure swing absorption (PSA) or prism membrane-based technologies. Although these methods can produce oxygen with up to 95% purity, units capable of supplying pure O_2 in the quantities involved in medical applications are large, noisy and require high electrical power. Furthermore, recent studies [3] have shown that the efficiency of O_2 concentration for PSA decreases steadily upon increasing the flow rate and period of use, raising serious questions regarding the reliability of this technology during unattended operation.

II. Oxygen Generation by Electrochemical Routes

A series of intriguing electrochemically-based strategies have been proposed over the past two to three decades to produce pure oxygen either by water electrolysis, or by the reversible reduction of O_2 from the atmosphere. Because of the high temperatures involved in solid oxide based devices, and the high volatility and general toxicity of non-aqueous solvents, the discussion to follow will be restricted exclusively to processes in aqueous electrolytes at room temperature.

In its most practical form, oxygen generation via water electrolysis relies on the use of an oxygen cathode (as opposed to the reduction of water, which produces hydrogen as a product) as the counter reaction [4]. Although from a strictly theoretical basis this type of water electrolysis should operate with very high efficiency, the iR losses and electrode overpotentials result in operating cell voltages of ca. 1.1 V at current densities of ca. 100 mA/cm^2 [4]. Specific power requirements for this type of technology are on the order of 180-200 W/kg O_2-day.

The second strategy is based on the reduction of oxygen from the atmosphere to produce superoxide (O_2^-) and/or peroxide (H_2O_2), which after migration through the electrolyte undergo oxidation at an anode to regenerate dioxygen [5-8]. At least three different methods have been explored to implement this general approach (see Table I in page 4). As indicated in that table, all these reactions do not involve scission or formation of O-O bonds, and, therefore, display much higher energy efficiencies compared to water electrolysis.

Direct pathways are based on the formation of H_2O_2 or O_2^-, in anionic or neutral forms (not shown in this diagram) at the cathode, and their subsequent oxidation at the anode via heterogeneous electron transfer processes involving simple electrode materials, e.g. metals, metal oxides and carbon [5].

TABLE I

ELECTROCHEMICALLY-BASED PATHWAYS FOR OXYGEN PURIFICATION IN AQUEOUS ELECTROLYTES

A. DIRECT PATHWAYS		
	CYCLE I	
a. Peroxide Route		**b. Superoxide Route**
$O_2 + H^+ + 2e^- \rightarrow HO_2^-$	Cathode	$O_2 + e^- \rightarrow O_2^-$
$HO_2^- \rightarrow O_2 + H^+ + 2e^-$	Anode	$O_2^- \rightarrow O_2 + e^-$
B. REDOX MEDIATED PATHWAYS		
	CYCLE II	
	$M + e^- \rightarrow M^-$	Cathode
	$M^- + O_2 \rightarrow [M\text{-}O_2]^-$	Solution Phase
	$[M\text{-}O_2]^- \rightarrow M + e^- + O_2$	Anode
	CYCLE III	
a. Peroxide Route		**b. Superoxide Route**
$M + 2e^- \rightarrow M^-$	Cathode	$M + e^- \rightarrow M^-$
$2M^- + O_2 + H^+ \rightarrow 2M + HO_2^-$	Solution Phase or Cathode	$M^- + O_2 \rightarrow M + O_2^-$
$HO_2^- \rightarrow O_2 + H^+ + 2e^-$	Anode	$O_2^- \rightarrow O_2 + e^-$

Redox-mediated, or indirect pathways, rely on the ability of a species M^- generated at the cathode to either bind O_2 reversibly, to form a solution-phase adduct $[M\text{-}O_2]^-$ (see Cycle II), or to react with O_2 to form unbound, dissolved O_2^- or H_2O_2 (Cycle III), which can then be oxidized at the anode to yield O_2 [6,7]. As indicated, these redox-mediated cycles are regenerative, i.e. the electrocatalyst returns to its original state after the full reaction sequence is completed. Furthermore, in the case of cycles of type III, M could either be in solution or irreversibly bound to the electrode surface.

Although from a strictly Faradaic viewpoint, the amount of charge required to "transfer" a given amount of O_2 would be twice for a two-electron (Cycles Ia and IIIa), compared to a one-electron process (Cycles Ib and IIIb), several factors must be considered in the development of a practical device.

i) The exchange current densities of the O_2/HO_2^- and O_2/O_2^- (Cycle I), as well as the selectivity of these processes, depend markedly on the nature of the electrode material and the pH of the aqueous electrolyte [9]. For example, parallel or sequential reactions that would lead to unwanted products include, the further reduction of peroxide to yield water or hydroxyl, and the dismutation of peroxide or superoxide. The selective and reversible reduction of O_2 to H_2O_2 proceeds readily in alkaline electrolytes on high purity carbon [10]. In acid media, however, and with only a few exceptions, most electrocatalysts reduce

O_2 via a series or parallel mechanism, involving the two-, and the clearly undesirable, four-electron pathways [9]. Furthermore, many of the most powerful molecular electrocatalysts are also capable of chemically decomposing and/or reacting irreversibly with H_2O_2 [10] leading to losses in performance.

ii) Solution-phase redox mediators generated at the cathode can be oxidized at the anode without reacting with dioxygen, giving rise to parasitic currents that will decrease the Faradaic efficiency of O_2 transfer.

iii) The rates of O_2 transfer in Cycle II are largely determined by the concentration of M in the media and by the diffusion coefficients of both M and $M\text{-}O_2^-$. Species of type M displaying high equilibrium constants for the formation of $M\text{-}O_2^-$, such as metal porphyrins and other macrocyles, are rather bulky; hence, their diffusion coefficients are small, ca. 10^{-6} cm^2/s [11]. Furthermore, their solubilities are not only moderate at best, but at higher concentrations tend to form aggregates which exhibit even lower mobilities.

It is, therefore, not surprising, that devices based on Cycle II, explored primarily by Aquanatics [6], could be operated at currents no larger than 1 - 2 mA/cm^2, before the (electrochemical) stability of the mediator was compromised. On these bases, the size and weight of a reactor capable of producing oxygen at the desired rates would be too large to be practical for portable applications. Some of the same arguments apply to processes based on Cycle III involving solution phase mediators, such as that described by Chillier-Duchatel and Verger [8], which uses 2,7-anthraquinone-disulfonate in solution phase as the reducing agent to generate peroxide from dioxygen.

iv) Parasitic currents of the type specific in ii) above can be eliminated by immobilizing M onto the electrode surface. This can be achieved by chemically derivatizing M and/or the electrode surface with functional groups that can form robust interfacial bonds without modifying the activity of the electrocatalyst.

v) Superoxide ion (O_2^-) is unstable in aqueous electrolytes at room temperature undergoing dismutation to yield H_2O_2 and O_2. Advantages and limitations of O_2^--based O_2 concentrators may be found in Ref. 8.

vi) In addition to kinetic hindrances for electron transfer at both interfaces, care must be exercised in the design of electrochemically-based oxygen concentrator devices to minimize solution phase iR losses.

Because of their inherent limitations, none of the electrochemical technologies described above have been further developed for medical or other uses.

III. Freshaire's Concept

As described in our original patent [13], Freshaire's novel electrochemical method for concentration and purification of dioxygen (O_2) at room temperature relies on the two-electron reduction of O_2 from air at a gas permeable cathode to yield H_2O_2, which then migrates through a solid polymer electrolyte (SPE) to a gas permeable anode, where it is oxidized to generate O_2 (see Fig. 1). The cell reactions in aqueous electrolytes are given in Table II below.

The electrodes are of the gas diffusion (GD) type, and incorporate Teflon-bonded high area carbon, either pure, or modified by a highly active, highly specific surface-confined electro-catalyst, attached to either side of the SPE membrane[14]. In addition to providing high ionic conductivities, and a rather effective barrier for the mixing of reactants, SPE-based reactors have many advantages over conventional liquid electrolyte systems. In particular, monolithic-type single cells as thin as 1 mm can be assembled using relatively known procedures, the lack of corrosive fluids minimizes problems with construction materials, and devices can tolerate rather high differential pressures.

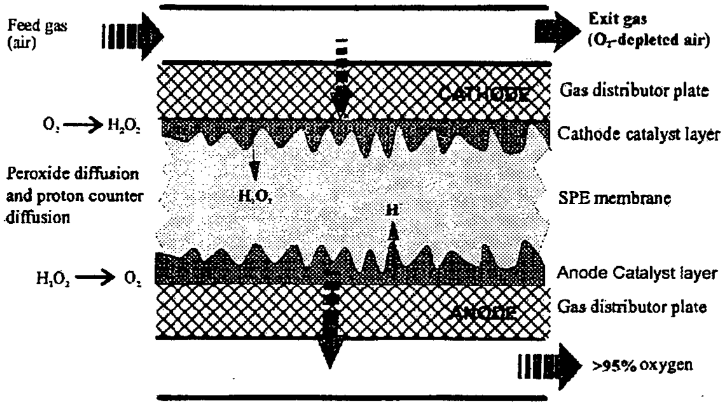

Fig. 1. Schematic diagram of Freshaire's approach for oxygen extraction from atmospheric air.

TABLE II

ELECTRODE REACTIONS IN FRESHAIRE'S CELL IN BASIC AND ACID MEDIA AND THEIR STANDARD POTENTIALS

Alkaline		
Cathode	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	$E^0 = -0.048$ V
Anode:	$HO_2^- + OH^- \rightarrow O_2 + H_2O + 2e^-$	
Acid		
Cathode:	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	$E^0 = 0.695$ V
Anode:	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	

These factors will be exploited to develop a versatile and efficient portable electrochemical oxygen concentrator (PECOC), which offers a number of advantages over other competing technologies, including portability, power efficiency, virtually noise-free characteristics and low weight. In addition, PECOC will benefit from continuing advances in SPE-based fuel cells, with which it shares many important commonalities.

B. Hypothesis

Freshaire's solid polymer electrolyte patented technology provides an expedient electrochemical means of producing nearly pure oxygen (> 98%) from the atmosphere under ambient pressure and temperature conditions with relatively low power requirements. Full development and optimization of catalysts, membranes and interfacial bonding methodologies will lead to the bipolar assembly of single monolithic units into an integrated Portable Electrochemical Oxygen Concentrator (PECOC). This unit will be capable of delivering 3 L/min of pure dioxygen and, thus, meet the requirements for home and ambulatory oxygen for medical applications and serve as a building block for much larger stationary units with potential industrial and military/medical. In particular, it could be readily adapted and integrated into a Life Support Trauma and Transport Platform (LSTAT) environment for battlefield combat casualty care, currently under development by the armed forces.

C. Overall Technical Objectives

The successful completion of the primary goals of this project relies on a full optimization of all materials and methods involved in this technology. Freshaire's process can, in principle, operate both in acid and alkaline media; however, several factors must be considered before assessing their viability.

i) Electrocatalytic materials displaying high activity for the selective reduction of O_2 to H_2O_2 in alkaline media are well-known and have been extensively studied [10]. Only minor modifications to established procedures may be required to incorporate such materials into suitable gas diffusion electrodes. In contrast, there are only very few catalysts capable of reducing O_2 to H_2O_2 in acid media without parallel or sequential processes that generate water as a product. Research in this area, however, has been very limited, since most of the effort over the years has focused on promoting the four-electron (4-e^-) reduction of O_2 to raise the efficiency of air-cathode-based fuel cells.

ii) Proton-exchange membranes, such as Nafion, are known to display higher ionic conductivities and higher chemical and electrochemical stabilities [14] than their far less developed anion-exchange counterparts [15].

iii) Carbon dioxide present in the air reacts with alkaline electrolytes to form sparingly soluble carbonates, which will form solids or gels that block both the membrane and the electrodes. It is conceivable that an alkaline-PECOC exposed to the atmosphere just prior to start-up may operate reliably for a few hours, which may be sufficient for emergency assistance. CO_2 in the cathode air feed could be removed using a low weight scrubber in combination with a blower. This approach, however, will increase the net volume, power requirement and maintenance frequency characteristics of the unit and ultimately limit its useful life.

6. BODY OF THE REPORT

A. Experimental Methods

I. Catalyst Preparation

a. Synthesis of Polymeric Electrocatalysts - Standard synthetic procedures were employed to prepare the monomeric phenanize (Phz) precursor, which was then reacted in the sequence shown in Fig. 2 to yield the desired polymeric product (PPZ). The advantage of this scheme is that a variety of R groups can be appended to the phenazine ring at the Friedel-Crafts alkylation step at the 4, 5, or 7 positions. This specific synthetic pathway leads to an all *anti* coupled polymer when 7-alkyl-2-aminophenazine is used as the monomer in the final oxidative polymerization. An all *syn* coupled product can be obtained by Friedel-Crafts alkylation following reduction of the nitro groups with the amino group at the 2-position of the phenazine ring directing alkylation to the 1, 3, or 6 positions. Then use of the 6-alkyl-2-amino-phenazine isomer leads to an all *syn* coupled polymer.

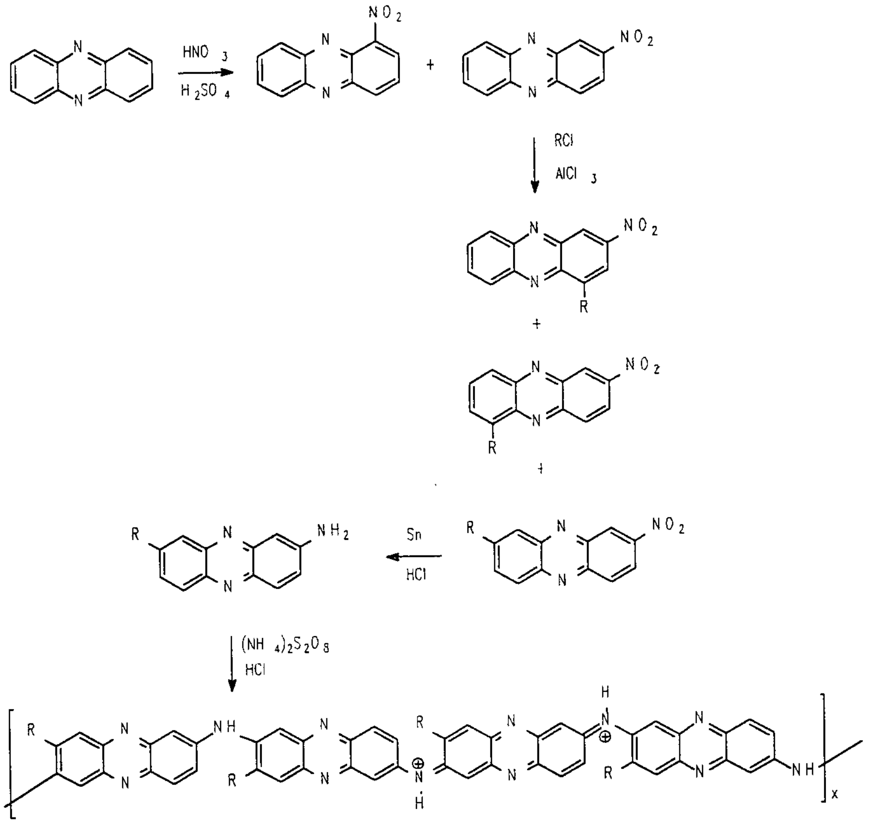

Fig. 2. Synthetic pathway for the preparation of a polymeric phenazine.

A copper modified polymer could be obtained by refluxing PPZ with an aqueous solution of $CuCl_2$.

b. Gold Dispersed on Graphite: Au dispersions on graphite of 1, 5, 20 and 50% Au weight-by-weight were prepared by borohydride reduction of an aqueous sodium tetrachloroaurate (Johnson Matthey) solution in the presence of high purity graphite powder. Ad-mixed catalysts, i.e. Au-ZnO/C and ZnO/C were made by mixing commercial ZnO powder with Au/C and C, respectively, under ultrasonic agitation to obtain a uniform dispersion, and then allowing the mixture to dry.

II. Electrode Preparation

The electrocatalytic activity of dispersed catalysts was examined by a variety of methods. For example, in the case of Au/C (1%) and the two polymeric species, the materials were mixed with an aqueous/alcoholic solution of Nafion under ultrasonic agitation. A drop of the suspension was then applied to the surface of a solid carbon electrode which was then allowed to dry to yield a macroscopic uniform film on the surface. In other instances, the materials were first mixed with XC-72R high area carbon then with mineral oil to produce a paste and then applied onto the tip of recessed (ca. 0.1 mm) pyrolytic graphite disk electrode ca. 0.2 cm^2 cross sectional area.

For reactor type measurements gas-permeable, (GP) Teflon-bonded type cathodes suitable for O_2 reduction (and, when applicable, O_2 evolution) were prepared by dispersing the catalyzed carbon powder in distilled water under ultrasonic agitation. The pH of the solution was then adjusted and a Teflon emulsion added to the slurry to induce, after further sonication and stirring, flocculation. The slurry was then filtered onto a hydrophobic carbon fiber paper and the resulting paste-like material pressed and then heat-treated to sinter the Teflon yielding a sturdy porous electrode. Finished electrodes were first die-cut to the required size and the catalyst layers impregnated with a prescribed loading of solubilized membrane (prepared by dispersing the membrane material in suitable solvents under pressure), and then air-dried to remove the solvents. Concurrently, sections of the ionomeric membrane were fully hydrated in distilled water and die-cut to size with all necessary perforations for alignment and manifolding. This last step was performed immediately prior to bonding to minimize dimensional changes that may occur due to changes in hydration during storage.

III. Electrochemical Methods

The assessment of electrocatalytic activity was made using cyclic voltammetry in both quiescent solutions and under forced convection using a rotating disk electrode in either sulfuric or phosphoric acid.

IV. On line Mass Spectrometry

The composition of the gas evolved at the anode of a prototype PECOC based on an Pt/Ir catalyst was determined by mass spectrometry using an Ametek-Dycor Q100-MA residual gas analyzer (RGA) operating in a turbo-pumped vacuum chamber at a base pressure of 6 x 10^{-8} torr (ionization beam current, 1 mA), while exposing the cathode to the ambient atmosphere. A schematic diagram of the experimental set-up is shown in Fig. 3. The PECOC, installed in a specially designed acrylic holder, was operated at either 21 or 42 mA . The volume of gas generated by the anode was measured by means of a *low friction* syringe as shown in the figure. Gas samplings were performed every 10 min for a total of 250 min. For each of the runs, the PECOC was allowed to operate for 10 min. with the leak valve closed. At the end of this period, the valve was opened just sufficient to allow a negligible amount of gas to enter the high vacuum chamber while collecting mass spectral data for 2 min. at which time the valve was closed. This procedure was repeated every 10 minutes until the syringe reached full capacity. The volume was then recorded, the current to the PECOC was interrupted and the leak valve opened to remove a pre-determined amount of gas from the syringe. Subsequently, the leak valve was closed and the final volume noted before resuming operation. This procedure was repeated as necessary to maintain the desired level of gas in the syringe. The O_2/N_2 ratio was calculated directly from the corresponding partial pressures measured from the mass spectrometer.

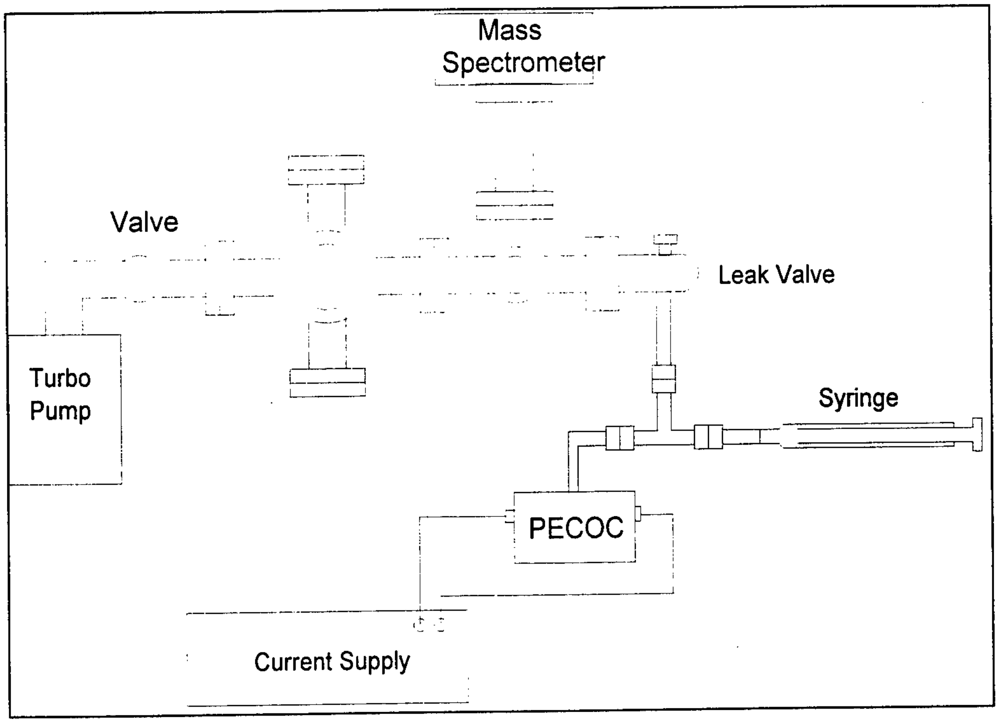

Fig. 3. Schematic diagram of the experimental set-up for O_2 determination measurements

B. RESULTS

I. Catalyst Screening

Except where otherwise noted the activity of all electrocatalysts was determined using the rotating disk (RDE) technique in acid aqueous electrolytes.

a. Au/C and polymeric catalysts

Two main conclusions emerged from polarization curves for dioxygen reduction using dispersed Au on graphite and the copper free polymeric catalysts:

i. The I vs. V curves were very reproducible with hardly any noticeable hysteresis between the scans in the positive and negative directions.

ii. The currents ascribed to oxygen reduction were found to be independent on the rotation rate of the electrode for scanning rate of 5 mV/s, i.e. the process appears to proceed under pure kinetic control even for the largest overpotentials examined

A comparison of the activity of the two types of catalysts using a rotating disk electrode at 2500 rpm is shown in Fig. 4. Unfortunately, it is not possible to determine which one of the two catalysts is more active, as the actual electrode area in contact with the electrolyte is not known with certainty. As may have been expected, however, the overall activity increased with the total amount on Au in the dispersion (see Table III).

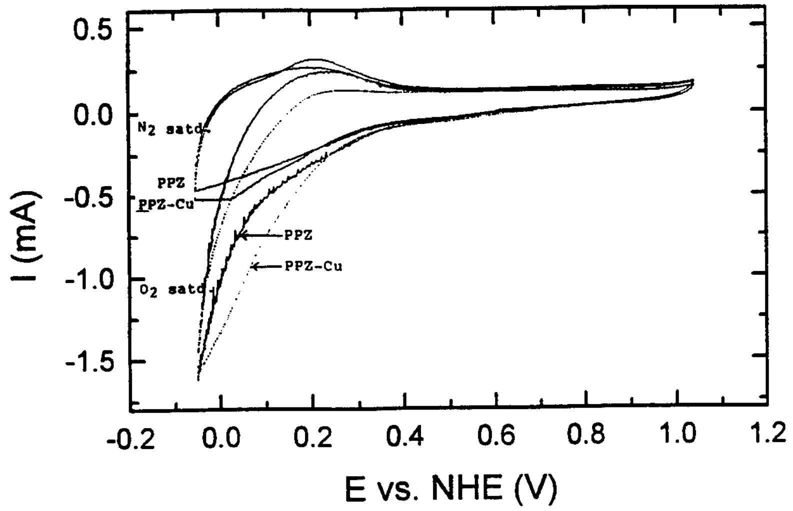

Fig. 4. Potential vs Current Curves for Oxygen Reduction on Au/C (◆) and PPZ (O) recorded with a RDE in 1 M H_2SO_4 at 25oC

TABLE III

Currents at 0.40 and 0.20 V obtained with a RDE for 5%Au/C and 50% Au/C in 1 M H_2SO_4 at various rotation rates.

Rotation Rate (rpm)	Current (mA) at 0.40 V		Current (mA) at 0.20 V	
	5% Au/C	50% Au/C	5% Au/C	50% Au/C
400	0.038	0.026	0.020	0.107
900	0.040	0.026	0.260	0.118
1600	0.043	0.026	0.303	0.122
2500	0.050	0.030	0.355	0.136
3600	0.065		0.443	0.154

b. Oxygen Reduction Catalyzed by Polyamino Phenazine in Phosphoric Acid Electrolytes

The electrocatalytic activity of polyaminophenazine acetate (PPZ, ICET, Inc) for the reduction of dioxygen was examined in 0.10 M H_3PO_4 solutions (Mallinckrodt reagent H_3PO_4 diluted with ultrapure water generated by a Barnstead EASYpure UV compact system) using a rotating Au ring-glassy carbon (GC) disk electrode (0.459 cm^2). For these experiments, a small drop of a 0.05% solution of PPZ in DMSO (ACS certified reagent) was placed onto the polished (α-Al_2O_3 0.05μ, BUEHLER Ltd. on a polishing cloth BUEHLER Ltd.) GC disk electrode (Pine Instrument Company). The solvent was then allowed to evaporate leaving a very thin film of the catalyst adhered to the electrode surface.

As reported by other workers, the overpotentials for hydrogen evolution and for oxygen reduction on a bare (non-catalyzed) GC electrode in acid electrolytes are very high. i.e. the onset for H_2 evolution in deaerated 0.10 M H_3PO_4 was found to be ca. –0.25V vs RHE and that for O_2 reduction in the O_2-saturated solution was ca. 0V vs RHE (see solid and dashed lines in Fig. 5, respectively).

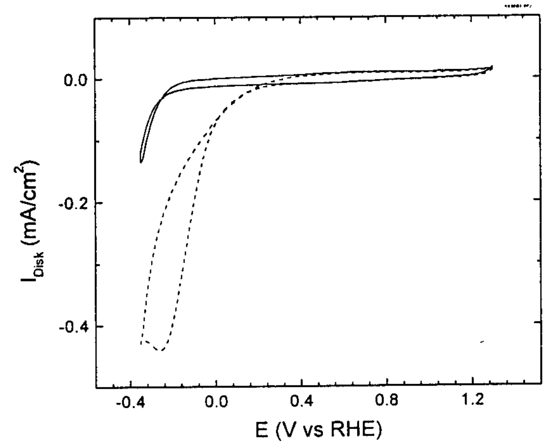

Fig. 5. Voltammogram of glassy carbon electrode in a stagnant N_2-saturated(solid curve) and a stirred O_2-saturated (dashed line, 100 rpm) 0.10 M Mallinckrodt AR H_3PO_4 solutions. Scan Rate: 50 mV/s.

A series of dynamic polarization measurements on the PPZ-modified GC disk of the Au/GC RRDE assembly were recorded in O_2-saturated 0.10 M H_3PO_4 prepared by purging oxygen for more than 1.5 hours at rotation rates in the range 100 to 2500 rpm at a scan rate of 10 mV/s (see Panel A, Fig. 6).

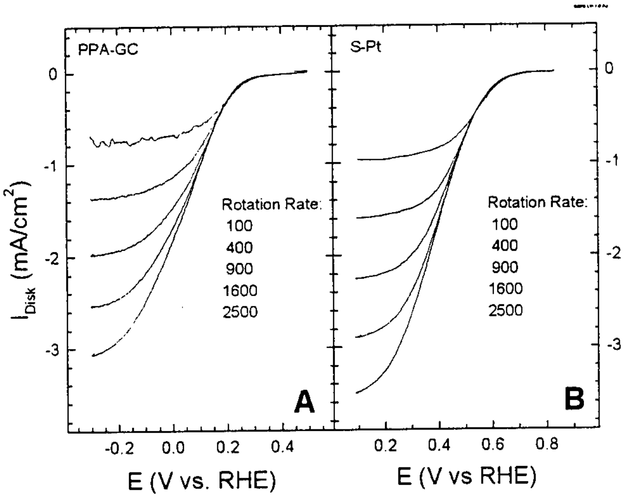

Fig. 6. Polarization curves for O_2 reduction on a PPZ-modified glassy carbon electrode (Panel A) and sulfur-modified Pt RDE electrodes (Panel B) in O_2-saturated 0.10 M H_3PO_4. Scan rate: 10 mV/s. Rotation rate: 100, 400, 900, 1600, 2500 rpm.

It may be concluded, based on the magnitudes of the limiting currents that the reduction of dioxygen on PPZ proceeds predominantly via a two-electron mechanism to yield hydrogen peroxide as the product. Unfortunately, attempts to measure peroxide oxidation currents using the concentric Au ring electrode yielded unreliable results, the causes of which are currently under investigation. The onset potentials for O_2 reduction were more positive than those observed on the bare GC, but more negative than those found for sulfur-modified platinum to be discussed in more detail below.

In cyclic voltammetry experiments performed in a 2 M H_2SO_4 quiescent solution the activity of the copper modified polymer in the form of an ink was found to be slightly better than that of the copper free counterpart (see Fig. 7).

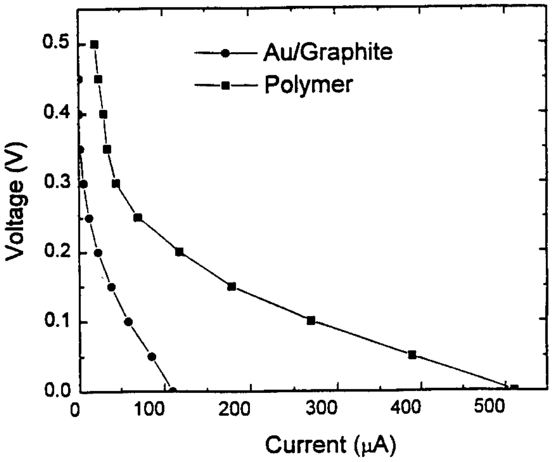

Fig. 7. Cyclic voltammograms obtained for graphite disk electrodes (area: 0.32 cm^2) coated with a film of PPZ and PPZ-Cu in 2 M H_2SO_4.

c. Modified Smooth Platinum

An exhaustive review of the literature identified copper as the only additive capable of promoting the rates of oxygen reduction to hydrogen peroxide on platinum in aqueous phosphoric acid electrolytes. Experiments were conducted to explore this effect in more detail using a Pt-Pt RRDE in 0.1 M H_3PO_4.

A series of measurements were performed in the neat electrolyte to better compare the electrocatalytic properties of Pt both in the absence and in the presence of Cu^{2+} in solution. Fig. 8, upper panel, shows a typical cyclic voltammogram for the clean Pt disk of the Pt-Pt RRDE in the potential range ca. 0.0 - 1.45 V vs RHE in nitrogen-purged 0.1 H_3PO_4 obtained as a scan rate of 50 mV/s. Virtually identical curves were obtained for the Pt ring of the same assembly as shown in the lower panel in this figure. As is well known, the symmetric features in the range 0 - 0.3 V are attributed to the adsorption/desorption of atomic hydrogen on Pt, whereas the rise and plateau in the range 1 - 1.5 V and the peak centered at 0.8 V in the scans in the positive and negative directions are due to the formation and reduction of a superficial layer of PtO_2, respectively. Evidence for the cleanliness of the electrolyte was obtained by rotating the electrode at open circuit for about 3 min. to allow possible (mostly organic) impurities to adsorb on the surface.The rotation was then stopped, and a new voltammogram acquired by scanning first in the negative direction. As shown by the results obtained (not shown here) only very minor changes were observed in the hydrogen adsorption/ desorption region, indicating that the surface had not been blocked by contaminants.

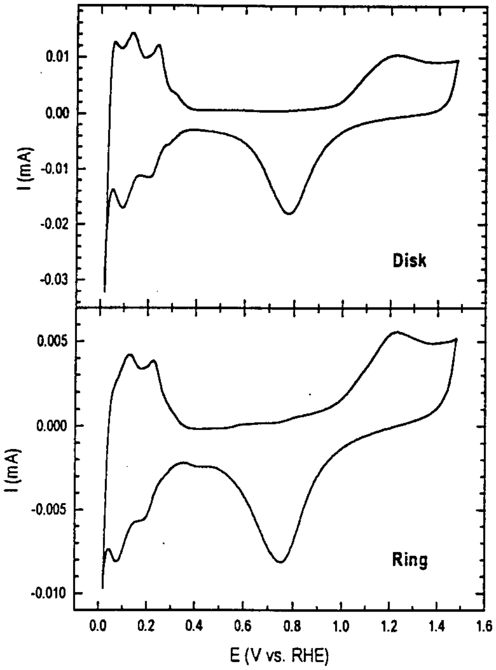

Fig. 8. Voltammograms for a Pt-disk (Upper panel) and Pt-ring (Lower Panel) of a Pt-Pt RRDE in nitrogen purged 0.1M H_3PO_4 at a scan rate 50 mV/s.

Figure 9 displays dynamic polarization curves for dioxygen reduction on the disk of the Pt-Pt RRDE at different rotation rates in the range 900 to 4900 rpm acquired at a scan rate of 10 mV/s during a scan toward negative potentials. Further aspects of these data will be discussed in subsection **d.** below.

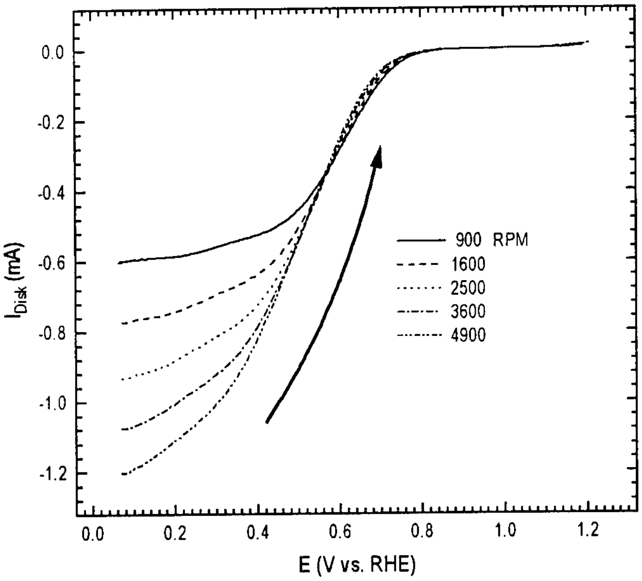

Fig. 9. Dynamic polarization curves for dioxygen reduction on the disk of the Pt-Pt RRDE at 10mV/s for different rotation rates

1. Underpotential Deposited Copper

Figure 10 shows the changes in the cyclic voltammetry induced by addition of a cuprous ion solution prepared by dissolving electrochemically a copper foil into the neat electrolyte. The concentration of Cu^{2+} was determined gravimetrically by weighting the foil before and after dissolution.

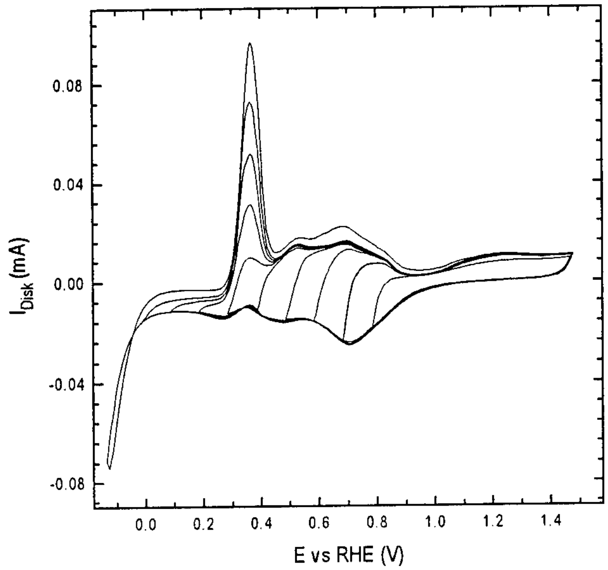

Fig. 10. Voltammetric curves for Cu UPD on Pt in 0.1M H_3PO_4 with 0.55 mM Cu^{2+}, scan rate: 50 mV/s.

As indicated, the presence of cuprous ions gives rise to marked changes in thevoltammogram including the appearance of rather well defined features in the double layer region of Pt, i.e. at potentials positive to copper bulk deposition as predicted by Nernstian thermodynamics. The ability of metal ions to undergo adsorption/charge transfer on foreign metal substrates at potentials more positive than bulk deposition has become known as underpotential deposition and has been the subject of numerous investigations.

A series of dynamic polarization curves involving the same Pt-Pt RRDE arrangement were performed in oxygen-saturated copper-containing 0.1 M H_3PO_4 solution with the ring held at 1.40 V vs RHE, a potential sufficiently positive for the oxidation of hydrogen peroxide to occur under purely diffusion control. A direct correspondance was found between the increase in the disk current and that in the ring current (see Fig. 11), providing evidence that the presence of Cu on the surface may catalyze hydrogen peroxide formation as was suggested in the literature.

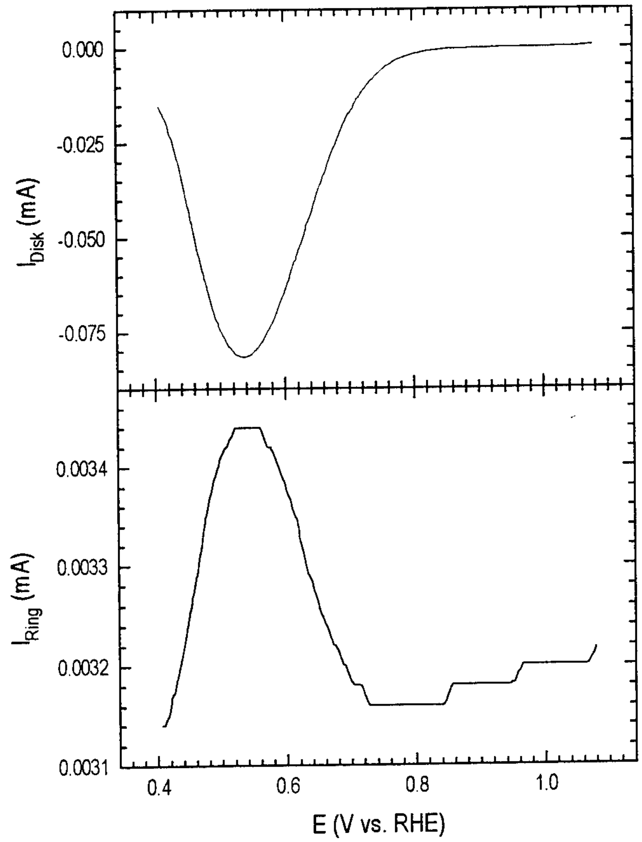

Fig. 11. Ring-disk dynamic polarization curve in oxygen-saturated copper containing 0.1 M H_3PO_4 with the ring held at 1.40V vs RHE. Scan rate: 10mV/s, rotation rate: 2500 rpm.

2. Sulfur-Modified Pt in Phosphoric Acid Electrolytes

The reduction of oxygen on both bare and S-modified Pt in 0.10 M H_3PO_4 solutions (J.T. Baker Ultrex II reagent H_3PO_4 diluted with ultrapure water generated by a Barnstead EASYpure UV compact system) was examined at room temperature with a Pt-Pt rotating ring-disk electrode (RRDE). For these experiments the Pt ring was set at +1.4 V vs RHE to oxidize quantitatively H_2O_2 generated at the disk. Measurements were performed in the dynamic polarization mode at scan rates of 10 mV/s using a Pine bi-potentiostat in a conventional three-compartment electrochemical cell.

The RRDE electrode was polished using α-Al_2O_3 0.5μ (BUEHLER Ltd.) on a polishing cloth (BUEHLER Ltd.). A series of cyclic voltammograms were recorded for the disk and the ring separately at a scan rate of 50mV/s in a nitrogen purged 0.10M H_3PO_4 solution, until features characteristic of the clean metal were obtained under rotation. Solutions were then saturated with O_2 by purging for 1.5 hours.

The sulfur modification of the Pt surface was achieved by placing a drop of a 50 mM Na_2S (reagent grade, Fisher Scientific) aqueous solution onto the Pt disk electrode without touching the ring. After thirty seconds the drop was removed by suction, the surface was then rinsed with pure water and the electrode introduced into the O_2 saturated electroyte. Prior to the dynamic polarization measurements, the ring was activated by cycling the potential between +0.04 and 1.5V vs RHE.

Fig. 12 shows disk (Panel A) and ring (Panel B) currents obtained during dynamic polarization measurements for oxygen reduction on a bare (dashed line) and sulfur-modified (solid line) Pt disk electrode at a rotation rate of 900 rpm. As clearly indicated, the sulfur modification gives rise to a marked increase in the amount of hydrogen peroxide collected by the ring compared to the bare Pt surface.

These data make it possible to determine quantitatively the yield of hydrogen peroxide generation at the disk via the formula:

$$Yield(\%) = \frac{I_{Ring}/N}{I_{Disk}} \times 100\% .$$

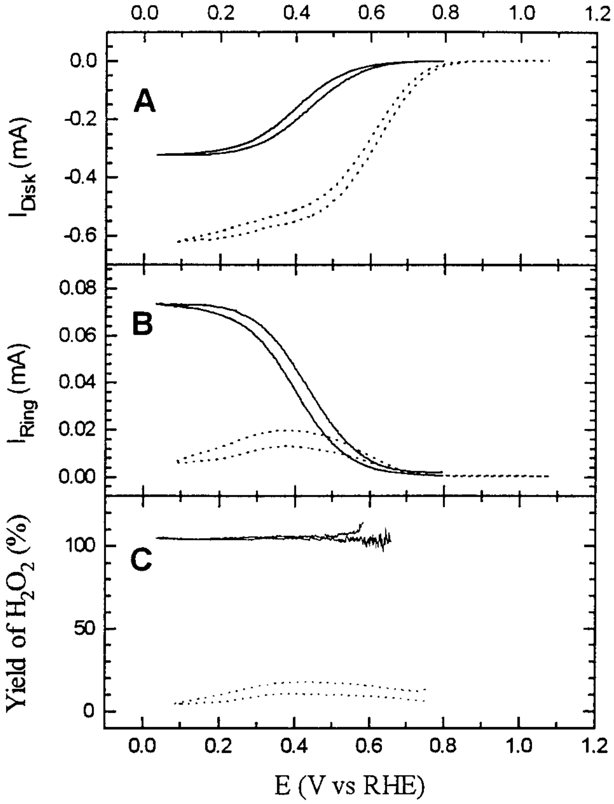

Fig. 12. Rotating Ring-Disk Dynamic Polarization Measurements for a Pt-Pt RRDE obtained with a bare Pt (dashed line) and sulfur-modified (solid line) Pt disk electrode in an O_2 saturated 0.10 M H_3PO_4 solution. PANEL A: Disk Current; PANEL B: Ring Current. PANEL C: Yield of Hydrogen Peroxide Generation at the Disk as a function of the applied potential.

d. Impurities in High-grade Commercial Phosphoric Acid

As shown in the previous two sections, the mechanistic pathways of oxygen reduction can be modified by the presence of species adsorbed on the electrode surface. The studies described in this section were aimed at assessing the purity of two high quality, commercially available, types of phosphoric acid :

1) Mallinckrodt AR (Lot No. 2796KJGL)
2) J. T. Baker Ultrex II reagent

Of particular concern was to determine whether contaminants present in these chemicals may be responsible for modifications in the intrinsic activity of bare platinum and gold surfaces for dioxygen reduction to peroxide. The information derived from these studies is also relevant to the quantitative analysis of RRDE data. To this end a series of voltammetric experiments both in quiescent and stirred deaerated 0.10 M H_3PO_4 solutions were performed using Au-Au and Pt-Pt RRDE's.

For the J. T. Baker Ultrex II reagent, using Pt electrodes, the voltammograms obtained with and without rotation were virtually the same and in excellent agreement with those attributed to clean Pt surfaces in this electrolyte. Although this behavior does not exclude the presence of impurities in the media, their effect of the electrochemistry (probably owed to their lack of affinity for Pt) is indeed negligible. In contrast, large differences could be observed in similar experiments involving Au electrodes as shown in Fig.13, where the curves in dashed and solid lines were obtained with (1600 rpm) and without rotation. In particular, although the curve recorded under stagnant conditions for Au in Mallinckrodt AR 0.10 M M H_3PO_4 display features characteristic of clean Au in this electrolyte, both an increase in the current was observed in the scan in the negative direction and a well-defined stripping peak at ca. 0.4 V vs RHE in the subsequent scan in the positive direction. Based on this overall behavior, copper may be identified as one of the impurities in the solution. No traces of copper could be found in similar experiments in 0.10 M M H_3PO_4 (J. T. Baker Ultrex II); however, measurements performed under rotation (see lower panel, Fig. 13) revealed distortions in the oxide, formation region with no rotation and the emergence of a prominent oxidation peak centered at ca. 1.5 V under rotation indicating that forced convection results in the accumulation of that species on surface. Although the very high potential required for its oxidation would suggest that this impurity is organic in nature, more experiments may be needed before a firm assignment can be made.

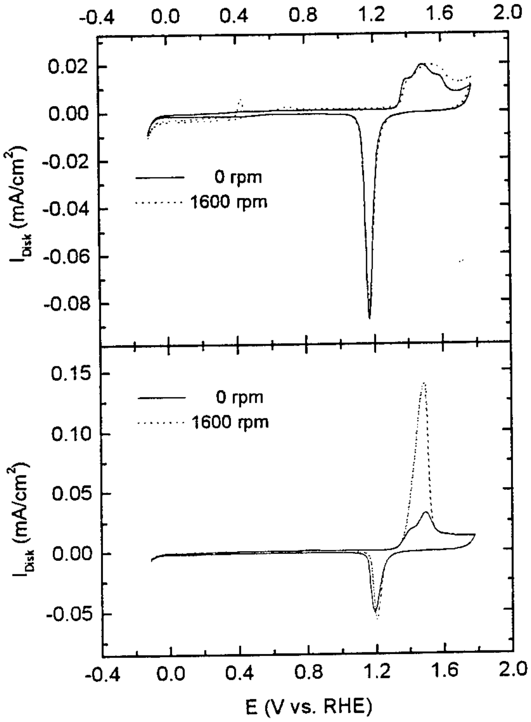

Fig. 13. Cyclic voltammograms of a Au disk electrode in N_2-saturated 0.10 M H_3PO_4 solutions prepared with Mallinckrodt AR (upper panel) and J. T. Baker Ultrex II (lower panel) H_3PO_4 with (dashed lines) and without (solid line) rotation (1600 rpm).

e. Single Cell Reactor Tests

Two Au-based catalysts 20 and 50 % w/w and PPZ/C were tested in a single cell reactor to asses their peroxide generation efficiency. Supported Pt (20% Pt/C) deliberately contaminated with Na_2S was also tested for comparison purposes. Gas diffusion type electrodes were fabricated using graphite fabric or paper as a substrate and used as cathodes in the reactor cell with platinized stainless steel plates as anodes. The electrolyte in the reactor cell was 1.0 M H_2SO_4 and Nafion membrane was used as separator. The electrolyte flow on the anode and cathode side was separated to allow sampling of catholyte. Permanganate titration of the catholyte sample was used for peroxide determination.

The results obtained indicated that both 20% PPZ/C (with air) and 20% Au/C (with O_2) display significant activity (~20-22%) for peroxide generation. The cell with 50% Au/C was operated with both air and O_2 flowing on the cathode side. With air flow, the peroxide generation was very minimal (only ~2%); with oxygen flow, the efficiency increased to ~ 14%. Enhanced oxygen partial pressure is most likely responsible for the efficiency increase. The electrode that gave poor performance was prepared using carbon paper substrate and was deliberately made very hydrophobic. Non-wetting characteristics of the active catalyst layer may also be at least partly responsible for its poor performance.

f. Performance Characteristics of a Prototype PECOC: Mass Spectrometry Studies

The data recorded with the system shown in Fig. 3 are compiled in Table IV. Also given in this table is the total charge passed, Q, in coulombs (C) determined from the current and the time of operation via the formula,

$$Q = \text{Current (mA)} \times \text{time (s)} \times 10^{-3} \qquad (1)$$

If is assumed that the only reaction that takes place at the anode is oxygen generation, the average number of electrons required to transfer a single oxygen molecule through the filter, n, may be calculated based on the volume of gas generated as measured from the syringe, yielding the values shown in Table V.

$$n = [\, Q \times 22.4 \times 10^3 \,] / [\, V(t) \times F \,] \qquad (2)$$

where V(t) is the volume of gas (mL) at time t, denoted, for simplicity, as O_2(exp) in Table V, 22.4 is the volume (in L) of a mol of gas under standard temperature and pressure and F is Faraday's constant, i.e. 96500 C/mol. As indicated in the table, n is ca. 4 electrons, providing evidence that the reaction at the anode may be represented as:

$$4H^+ + O_2 + 4e^- \Rightarrow 2H_2O \qquad (3)$$

It should be stressed that the amount of carbon dioxide was negligible and unchanged during the entire run. This type of test will be implemented for a PECOC working on a two-electron based process.

TABLE IV

Total Charge, O_2/N_2 Ratio, Experimental O_2 Volume,
Number of Electrons per Elementary O_2 Transfer Event (n)

Time t (s) x 10^{-2}	Current i (mA)	Charge[a] Q (C)	O_2/N_2 [b] (m/z=31.9)/(m/z=28)	O_2 (Exp) V(t) (mL)	n[c]
0	0	0.0	-	-	-
6	42	25.2	1.64	1.5	3.90
12	42	50.4	1.67	3.0	3.90
18	42	75.6	1.72	4.2	4.18
24	42	100.8	3.82	5.6	4.18
30	42	126.0	4.02	7.2	4.06
36	21	138.6	8.38	7.9	4.07
42	21	151.2	8.63	8.7	4.03
48	21	163.8	8.80	9.5	4.00
54	21	176.4	8.92	10.2	4.01
60	21	189.0	14.87	11.0	3.99
66	21	201.6	14.82	11.8	3.97
72	21	214.2	14.97	12.5	3.98
78	21	226.8	15.26	13.2	3.99
84	21	239.4	18.46	14.1	3.94
90	21	252.0	18.02	14.8	3.95
96	21	264.6	18.53	15.5	3.96
102	21	277.2	18.41	16.3	3.95
108	21	289.8	16.70	17.1	3.93
114	21	302.4	16.71	17.8	3.94
120	21	315.0	16.62	18.6	3.93
126	21	327.6	16.73	19.3	3.94
132	21	340.2	18.85	20.2	3.91
138	21	352.8	19.28	21.0	3.90
144	21	365.4	19.63	21.7	3.91
150	21	378.0	19.80	22.3	3.93

a. $Q = i \times t \times 10^{-3}$

b. Evaluated directly from mass spectral data.

g. Demonstration of 10-cell Oxygen Concentrator

Although beyond the research program proposed in the original six months program, a demonstration unit was designed and constructed based on a 4-electron as opposed to a 2-electron oxygen transfer pathway. The work involved:

- Procurement of a set of fuel cell hardware off the shelf from Dais Corporation;
- Modification/adoption of the hardware to the requirements of the oxygen generator;

- In-house fabrication of electrodes, MEAs, flowfield/current collector, gaskets and other ancillaries;
- Assembly and testing of a single cell oxygen generator;
- Assembly of the 10-cell oxygen generator stack, its testing and demonstration.

The oxygen generator stack was to operate, by the nature of its hardware design, by naturally convective air flow (air-breathing mode). An external air blower was used, however, to force air into the device and thus enhance the stack performance. Some dimensional and performance characteristics of the stack under forced air operation are:

- Dimension (external) : 8" x 4.5" x 3.5"
- Weight : ~ 9 lbs
- Active electrode area : 6" x 3"
- No of cell in stack : 10
- Max operative current : 20 A at 33 V*
- Vol. of O_2 produced : 850 mL/min

- A single cell using the same hardware showed a cell voltage of ~1.3 V while operating at 20 A; the 10-cell stack was therefore expected to operate at ~ 13-15 V at the same current with the allowance of some IR loss. Hardware-related problem, however, resulted in unusually high voltage drop (~18 - 20 V) in the stack. The hardware design required the use of several layers of spot-welded stainless steel screens for current collection on both anode and cathode sides. Cumulative contact resistance of these current collectors perhaps contributed most to the stack resistance.

7. CONCLUSIONS

(i) The polymer-based catalyst (PPZ/C) displays an activity for oxygen reduction to hydrogen peroxide in aqueous acidic electrolytes comparable to that of gold dispersed on graphite, Au/C. Incorporation of metal ions into the polymer may lead to further improvements in activity.

(ii) Various aspects of the operation of a highly efficient PECOC unit, at oxygen generation levels comparable to those required for military medical applications were demonstrated using modified hardware procured commercially.

(iii) A new class of surface modifiers for platinum has been discovered capable of promoting a highly efficient, highly selective, reduction of dioxygen to peroxide in acid electrolytes. This could open new prospects not only for a two-electron PECOC device, but also for the production of hydrogen peroxide for more general applications.

More work will be required to optimize all electrochemical components of PECOC before full optimization in terms of performance and long term reliability could be achieved.

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9. APPENDICES

a. Acronym

FIA-ED	Flow injection analysis with electrochemical detection
GD	gas diffusion (electrode)
HAC-GPTB	high area carbon-based, gas- permeable, Teflon-bonded (electrode)
LPM	liters per minute
PECOC	portable electrochemical oxygen concentrator
RDE	rotating disk electrode
RRDE	rotating ring-disk electrode
SPE	solid polymer electrolyte

b. Symbol Definition

F = Faraday's constant

n = net number of electrons transferred,

$C(O_2)$ = concentration of O_2 (mol/cm^3)

ν = kinematic viscosity (cm^2/s),

D = diffusion coefficient (cm^2/s).

E = potential

i = current

ω= rotation rate (rad/s)

i_k = *effective* kinetic current

$B = 0.620nFC(O_2)D^{2/3}\nu^{-1/6}$

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