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mise to safety of the lithium battery, depending on the conditions of abuse. The self-heating process in a lithium battery, initiated under abusive conditions which can eventually lead to a thermal runaway, does contain a number of different contributions. Analyzing these contributions shows that adding 2-MeTHF (cyclic ether) to a LiAsF_6 electrolyte containing a mixture of cyclic esters as solvents, lowers the initiation temperature of the exothermic thermal decomposition of the electrolyte from a temperature above to a temperature below the melting point of lithium. Since the reaction between molten unpassivated lithium and the electrolyte will cause significant heating, having the thermal decomposition occur first, will make this latter process more important with respect to battery safety. The higher heating rate associated with the thermal decomposition of the LiAsF_6 electrolyte containing esters only, as compared to the same electrolyte with ether added, is less important since these high heating rates occur at temperatures where other processes are already dominant. Replacement of LiAsF_6 by LiCF_3SO_3 (triflate salt), raises the initiation temperature for thermal decomposition substantially above the melting point of lithium, making the thermal decomposition of this electrolyte less important with respect to battery safety. However, this electrolyte has shown very poor cycling efficiency in the lithium battery of interest. Oxidizing LiAsF_6 electrolytes with cyclic ester/ether solvent mixtures which occurs during battery overcharge causes some further lowering of the thermal

stability temperature. Since these electrolytes already have a thermal stability temperature below the melting point of lithium, the oxidation further emphasizes the importance of electrolyte thermal decomposition in the self-heating process.

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Synthesis of Hydrogen Peroxide in a Proton Exchange Membrane Electrochemical Reactor

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ABSTRACT

Humidified oxygen was reduced to hydrogen peroxide at the cathode in a proton exchange membrane electrochemical flow reactor. The optimum conditions for peroxide generation were determined as a function of the applied voltage, electrode materials (gold, graphite, and activated carbon powders), catalyst loadings, reactant flowrates, and pressure. Measured and calculated quantities included cell current, peroxide concentrations, and current efficiencies.

The synthesis of hydrogen peroxide in a proton exchange membrane (PEM) electrochemical flow reactor was explored. This study was undertaken as a part of an overall scheme to study the paired synthesis of ozone and hydrogen peroxide in the same PEM reactor. The research methodology for the paired synthesis has been split up into four reaction systems: 1, water electrolysis which involves oxygen evolution at the anode and hydrogen evolution at the cathode; 2, ozone + oxygen evolution at the anode and hydrogen evolution at the cathode; 3, oxygen reduction at the cathode (leading to hydrogen peroxide synthesis) and oxygen evolution at the anode; and 4, simultaneous synthesis of ozone and hydrogen peroxide.

Preliminary studies on the first two reaction systems have been conducted.¹ This paper summarizes the investigation of the reduction of oxygen at the cathode leading to the synthesis of hydrogen peroxide while generating oxygen at the anode (reaction system 3). Although there have been investigations on the electrochemical synthesis of hydrogen peroxide in aqueous electrolytes (acidic and basic),²⁻⁵ to the authors' knowledge, no information exists on the synthesis of hydrogen peroxide using pure water and oxygen as reactants and a proton exchange membrane as the electrolyte.

The optimum conditions for electrochemical peroxide generation were determined as a function of the applied voltage, electrode materials, catalyst loadings, reactant flowrates, and pressure. Measured and calculated quantities included cell current, peroxide concentrations, and current efficiencies.

Experimental

A description of the electrochemical reactor and the flow system used in the experimental investigations are described elsewhere.¹ A Nafion[®] 117 membrane (du Pont) was used as the electrolyte for

all experiments. The cathode materials included powders of activated carbon (Aldrich Chemical), gold (Aldrich Chemical), and graphite (Asbury graphite mills) which were used as supplied by the manufacturer (*i.e.*, without any pretreatment procedures). The electrode assemblies used in this work were made by depositing a mixture of the catalyst powder and Teflon[®] (TFE, du Pont) onto the surface of the membrane at an appreciably high temperature and pressure. The fuel cell division of Treadwell Corporation (Thomas-ton, CT) which is now incorporated into U.S. Fuel Cells Manufacturing Incorporated, located in West Palm Beach, FL, fabricated these membrane electrode assemblies (M&Es) according to our specifications. The anode for all the experimental runs consisted of a platinum black (fuel cell grade)/TFE mixture which was deposited onto the membrane in a similar fashion. The platinum loading for each assembly was maintained at 4 mg/cm² with a 30 weight percent (w/o) TFE binder. The projected electrode area for both the anode and the cathode was 13 cm². This M&E assembly was sandwiched between a carbon fiber paper (Toray Industries) on the cathode side and a platinum mesh (52 mesh, Fisher Scientific) on the anode side which were used as current collectors.

Experimental procedure.—Humidified oxygen (Cryodyne Technologies) at 15 psig (2 atm) and room temperature was fed to the upper port of the cathodic section of the reactor at a flowrate of 100 cm³/min via a gas washing bottle containing deionized water. Deionized (18 M Ω) water at atmospheric and room temperature was fed to the anodic section of the reactor at a flowrate of 28 liter/h.

A fixed potential was applied to the reactor using a dc power supply (Nobatron, Norwalk, CT). The stream leaving the cathode was analyzed for H₂O₂ after the reactor reached a steady-state current of + or -0.1 A for at least 20 min. H₂O₂ concentrations were measured colorimetrically with self-filling ampuls (CHEMetrics, Calverton, VA) containing ammonium thiocyanate and ferrous iron in acid solution. Hydrogen peroxide oxidizes the ferrous iron into

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the ferric state resulting in the formation of a red thiocyanate complex. The intensity of the red color is directly proportional to the peroxide concentration in the sample.

Results and Discussion

The oxygen flow rate and oxygen pressure were varied from their base values of 100 cm³/min and 15 psig, respectively, to determine qualitatively, their influence on the dependent variables. The effect of varying the oxygen flowrate from 50 to 250 cm³/min at 15 psig showed no significant change in the measured cell current or the peroxide concentrations when the cell voltage varied from 0.0-4.0 V for all the three powders used. At a set voltage and flowrate (100 cm³/min), varying the oxygen pressure from 0-15 psig resulted in marginally higher cell currents at 0 psig. However, the peroxide concentrations at 0 psig were lower than those at 15 psig at the same applied cell voltage. A higher oxygen pressure was more selective for the two-electron process of oxygen reduction leading to peroxide formation than the four-electron process leading to water formation. This phenomenon could be occurring due to a lower migration rate of the H⁺ ions coming from the anode through the membrane at higher oxygen pressures. Again, this phenomena was observed for all the three powders that were used.

Three different powders, gold, graphite, and activated carbon, were tested for the synthesis of hydrogen peroxide. The gold M&E had a 2 mg/cm² loading and 10 or 20% TFE binder. The graphite M&E had 10 mg/cm² loading and also had 10 or 20% TFE binder. The activated carbon M&E also had a 10 mg/cm² loading, but was tested only with 20% TFE binder.

Figure 1 is a bar chart which compares the maximum hydrogen peroxide concentrations using these five different catalyst configurations and the potentials and currents at which the maximums were obtained. The graphite powder showed the best results in terms of the maximum peroxide concentration obtained. The gold and graphite M&E's with 20% TFE produced slightly higher hydrogen peroxide, but had a lower cell current as compared to the electrodes possessing 10% TFE. Increasing the percentage of TFE increases the hydrophobicity of the electrode assembly and thus allows more of the gaseous reactant to reach the electrode surface by repelling the products formed. The increased percentage also leads to an increase in the electrode resistance thus resulting in a slightly lower cell current. These phenomena were also observed by Ridge *et al.*⁶ while studying oxygen reduction on a gas fed porous electrode attached to a proton exchange membrane.

Figure 2 shows polarization plots for two different TFE loaded graphite/Pt M&E's. The graphite loading was 10 mg/cm² and the TFE percentage was 10 or 20%. The Pt side of the M&E was used as the anode and had a loading of 4 mg/cm². Appreciable current densities (greater than 150 mA/cm²) were observed at about 2.5 V. The currents increased linearly with the applied voltage indicating that the system was under a combination of kinetic and ohmic control. At voltages less than 3.0 V, the cell currents were lower for the M&E with 20% TFE binder. However, at potentials above 3.0 V, the cell currents for the 20% TFE binder M&E were higher. This

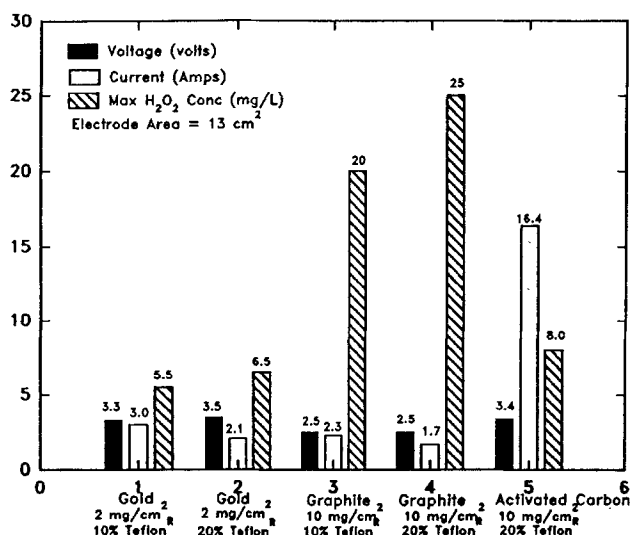


Fig. 1. Comparison of the maximum hydrogen peroxide concentrations obtained using different electrocatalysts and the potentials and cell currents at which they are obtained.

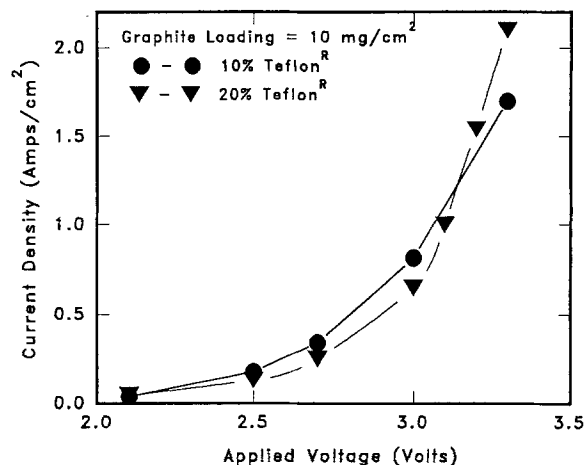


Fig. 2. A steady-state polarization plot using a graphite/platinum black M&E assembly.

could be due to the mass transport limitation of oxygen to the membrane electrode assembly within the less hydrophobic 10% M&E.

Figure 3 shows that the highest hydrogen peroxide production was at 2.5 V with the 20% TFE electrode yielding a slightly higher concentration. The concentration of peroxide dropped rapidly after 3.0 V. It should be noted that although there was some electrochemical activity within the reactor at potentials below 2.5 V, the observed steady-state current densities were very low (<46 mA/cm²) and hence the volume of the products formed were too small to be analyzed for H₂O₂.

A graphite membrane electrode assembly that previously generated high hydrogen peroxide concentrations during oxygen reduction was operated with nitrogen and oxygen feeds at potentials below 2.0 V. Figure 4 shows the polarization behavior under such conditions. While an applied voltage of 1.1 V was required with an oxygen feed to obtain a minimum current density of 0.75 mA/cm² (the lowest measurable current density from the power supply), a voltage of 1.8 V was required to obtain the same minimum current density under a nitrogen feed. This suggests that at potentials between 1.1 and 1.8 V a 100% current efficiency can be obtained for oxygen reduction on this electrode material.

Although the current efficiencies for oxygen reduction were 100% at potentials below 1.8 V, the volume of products obtained at these potentials was too small to be analyzed for hydrogen peroxide. For example, at 1.7 V, a steady-state current density of 12 mA/cm² was obtained and if a 30% current efficiency for H₂O₂ production is assumed, it would require an impractical 105 h of continuous reactor operation to obtain just 4 ml of the reaction products. Further, in the overall scheme to study the paired synthesis of ozone and hydrogen peroxide, the PEM reactor will be operated at potentials >3.0 V where the anodic evolution of ozone is favored.¹ Since peroxide production was observed at all potentials, (a phenomena that was observed with all the electrocatalysts examined) it is anticipated that the simultaneous synthesis of ozone and hydrogen peroxide is possible.

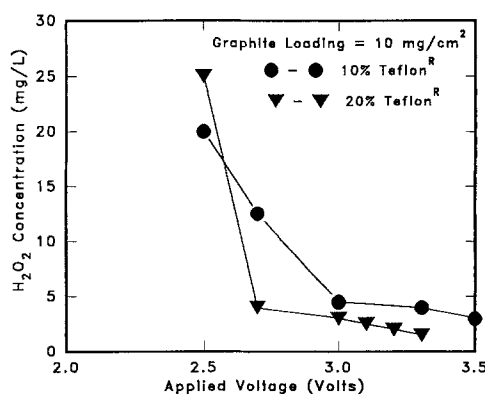


Fig. 3. Hydrogen peroxide concentration as a function of the applied voltage.

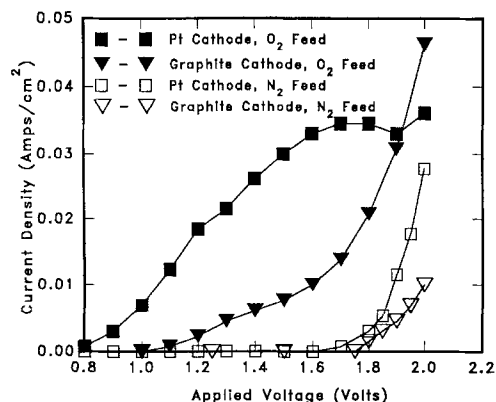


Fig. 4. Steady-state polarization plots of graphite and platinum black cathodes at potentials below 2.0 V with oxygen and nitrogen feeds.

At potentials above 2.0 V (not shown in Fig. 4), the M&E with a nitrogen feed displayed a similar trend in polarization behavior as compared to the M&E operating with an oxygen feed. The current densities obtained at different applied potentials above 2.0 V with a nitrogen feed were lower by about 1 A, as compared to the oxygen feed. This suggests that oxygen reduction is proceeding at a limiting rate alongside hydrogen evolution at potentials greater than 2.0 V. Poor oxygen reduction kinetics on graphite and mass-transfer limitations of oxygen gas to the membrane electrode interface led to the relative decrease in oxygen reduction currents as compared to hydrogen evolution currents.

Figure 5 shows a plot of the current efficiency for hydrogen peroxide production vs. applied voltage. The current efficiency was a maximum at 2.5 V for the electrode with 20% TFE and 2.7 V for the electrode possessing 10% TFE. The current efficiencies dropped rapidly beyond these potentials indicating a very narrow potential window for the maximum production of hydrogen peroxide.

When a platinum cathode was operated at potentials below 2.0 V (Fig. 4), an applied voltage of 0.8 V was required under an oxygen feed to obtain a minimum current density of 0.75 mA/cm², while a voltage of 1.7 V was required to obtain the same current density under a nitrogen feed. This suggests that at potentials between 0.8 and 1.7 V, a 100% current efficiency was obtained for oxygen reduction on this electrode material. A limiting current plateau was observed when the M&E was run with an oxygen feed at voltages between 1.6-1.9 V which probably corresponds to the four-electron reduction of oxygen to water. At potentials beyond 2.0 V (not shown in Fig. 4), hydrogen evolution causes a sharp rise in current densities for both, the oxygen and nitrogen feeds. Similar to the graphite cathode, current densities at the platinum cathode with an oxygen feed were always marginally higher (25-5%) than with a nitrogen feed suggesting that oxygen reduction was proceeding along with hydrogen evolution. Small amounts of hydrogen peroxide (1 mg/liter) were detected at all potentials >2.3 V. This means that the two-electron reduction of oxygen to hydrogen peroxide occurred simultaneously with the four-electron reduction of oxygen to water.

Conclusions

Three different powders, gold, graphite, and activated carbon, were investigated for the continuous production of pure hydrogen peroxide in a proton exchange membrane electrochemical flow

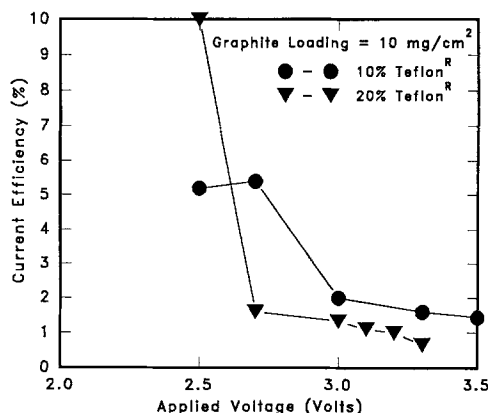


Fig. 5. Current efficiencies for hydrogen peroxide production as a function of the applied voltage.

reactor. The maximum peroxide concentrations (25 mg/liter at 2.5 V with a current efficiency of 10%) were obtained using the graphite powder at a catalyst loading of 10 mg/cm² with 20% TFE binder. However, as Fig. 1 shows, the maximum peroxide concentrations obtained on the gold and the carbon powder are at a considerably higher cell voltages than those obtained using the graphite electrode. This phenomenon will be of importance when the authors investigate the paired synthesis of ozone and hydrogen peroxide (reaction system 4) as the evolution of ozone is favored at higher potentials (>3.0 V¹). Hence, although the graphite powder appears to be the best electrocatalyst among the three materials investigated in this system, it may not be the most favorable material for the paired synthesis of the oxidants.

Further experimental investigations are being conducted on the synthesis of hydrogen peroxide. This includes the study of a gold loading of 4 mg/cm² as well as the examination of the three powders loaded onto the carbon fiber paper as opposed to the membrane.

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