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Paper Session III-A - Electrolytic Oxygen Enrichment Using Supernoxide Ion in a Solid Polymer Membrane Electrolyte

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Electrolytic Oxygen Enrichment
Using Superoxide Ion in a
Solid Polymer Membrane Electrolyte

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Abstract

Electrochemical cells are among the technologies under consideration for gaseous oxygen concentration or enrichment in both aerospace and civilian applications. Current electrochemical technology involves the electro-reduction of molecular oxygen, O₂, to water at one electrode, and the electro-oxidation of water to oxygen at the other. In terms of the overall chemical mechanism, this is a 4-electron, 4-proton process.

From an economic point of view, one would like to use as little energy as possible to effect oxygen transport. The simplest possible mechanistic scenario would be if the O₂ reduction product is the superoxide ion, O₂⁻, involving only a single electron exchange:



Superoxide anion can be produced electrochemically via reduction of O₂ in an organic aprotic solvent, such as dimethyl formamide or acetonitrile. Moreover, production of superoxide via electrolysis is electrochemically reversible (i.e., the forward and reverse reaction is so rapid that it proceeds under diffusion control near the thermodynamic potential). Considerable energy savings may be realized if electrochemical O₂ transport could be performed using superoxide ion.

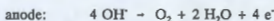
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In the mid 1980's the National Aeronautics and Space Administration - JFK Space Center conducted a study on the use of air depolarized alkaline electrolysis as a means of producing ultra high purity oxygen for propulsion applications [1]. While O₂-enriched air may not be necessary or economical for civilian transportation, the basic process of selective removal or concentration of oxygen from one flow stream to another can have a number of applications in the industrial sector. For example, in the natural gas business, selective O₂ pumps can control reformer reactor conditions during methane decomposition, and reduce nitrogen oxides resulting from methane combustion.

In May of 1990, the University of Central Florida granted an in-house research grant to

FSEC to investigate the possibility of using electrolytic methods for oxygen concentration. Based on their earlier work, the project was also joined by NASA as part of their Technology Utilization program. In the first phase of the project, the feasibility of the oxygen enrichment concept was demonstrated using solid polymer electrolytes. Many ion exchange polymers were evaluated with respect to their performance for electrochemical pumping of oxygen. DuPont's Nafion™ 117 was selected as the bench-mark membrane material due to its relatively low cost, high ionic conductivity, long-term stability and availability.

While a sulfonated polymer membrane certainly looks different from an aqueous alkaline solution, functionally they can be quite the same. In the alkaline electrolytic system, the desired electrode reactions were:



The two reactions are opposites of each other; thus the net result is the transport of O_2 from one side of the cell to the other. In acidic electrolyte, the two half-cell reactions would be:



O_2 is electro-reduced to water at one electrode, and then water is electro-oxidized to oxygen at the other. This also results in net transport of oxygen across the cell. The electrochemistry is the same whether it is done either with an acidic solution, or by using a specialized organic solid polymer membrane that is proton-conducting. Note that in either case, alkaline or acidic, the oxidation state of each oxygen atom is lowered from 0 to -2 at the cathode, and raised back from -2 to 0 at the anode. Thus for each diatomic molecule of oxygen gas to be delivered, four electrons must be transferred at both of the electrodes.

In the course of the early work, it was discovered that it may be possible to achieve a substantial improvement as to the operation and energy consumption of the electrolytic O_2 -pumping cells. From an economic point of view, one would like to use as little energy as possible to effect oxygen transport, which means minimum voltage at maximum current. The energy consumption of the cell per mole of O_2 would be

$$E = QV = nFV,$$

where E = energy per mole of O_2

Q = total charge transferred per mole

V = cell voltage

n = number of electrons transferred per molecule

and F = Faraday's constant, or 96,485 Coul/mole.

One can estimate the probable cell voltage necessary to drive an electrochemical O_2 -pump by looking at the current-voltage curves for the respective half-cell reactions. This is shown

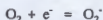
in Figure 1 for an acidic electrolyte system. The O_2 concentrator voltage is made up from the anode voltage in the electrolysis mode, and the cathode voltage is the galvanic, or fuel cell mode. Thus is one knows how the cell performs as an electrolyzer and also as a fuel cell, one can estimate how the cell will perform as an O_2 pump. For the Nafion membrane system, the electrolyzer voltage will lie around 1.75 V [2]; in the fuel cell, the operating voltage is about 0.8 V [3]. There is also the H_2 electrode polarization to deal with, but that is a very fast reaction and can be neglected for the present. The equation is

$$V_e - V_f - V_{H_2} = V_o$$

Thus one can expect an operating cell voltage on order of 1.0 V.

Another key point is that E is directly proportional to n, which is determined by the reaction stoichiometry. For the O_2 electro-reduction reactions described above, $n=4$.

It is not absolutely necessary that four Faradays of charge must be used to electrolytically move oxygen. Actually any oxygen species that is formed as a result of charge transfer onto O_2 , remains soluble in the electrolyte, and is electrochemically reversible can be used as the mobile agent. The simplest possible (and most desirable from an energy point of view) scenario would be if $n=1$, where the resultant reduction product is superoxide ion, O_2^- :



At constant voltage, the energy requirement for oxygen transport would be cut 75 % if superoxide could be used as the mobile agent.

Superoxides do indeed exist; they are mainly known in the form of alkali metal superoxides, MO_2 , where $M=K, Rb, \text{ or } Cs$ [4]. It is also possible to make tetraalkyl ammonium superoxides involving a solid-solid metathesis reaction between the alkali metal superoxide and the alkyl ammonium chloride in liquid ammonia [5,6]. The superoxide anion itself can be produced electrolytically, via reduction of O_2 in an organic aprotic solvent, such as dimethyl formamide, DMF, or acetonitrile, CH_3CN . Moreover, production of superoxide via electrolysis is electrochemically reversible (i.e., the forward and reverse reaction is so rapid that it proceeds under diffusion control near the thermodynamic potential). This is shown in Figure 2.

The peak-to-peak voltage is only 210 mV. Therefore, in comparison to aqueous systems, one can expect four-fold increase in O_2 -pumping on an electrical current basis, and a similar drop in voltage. Work is in progress to ascertain whether these energy savings in electrolytic O_2 transport can be achieved.

References

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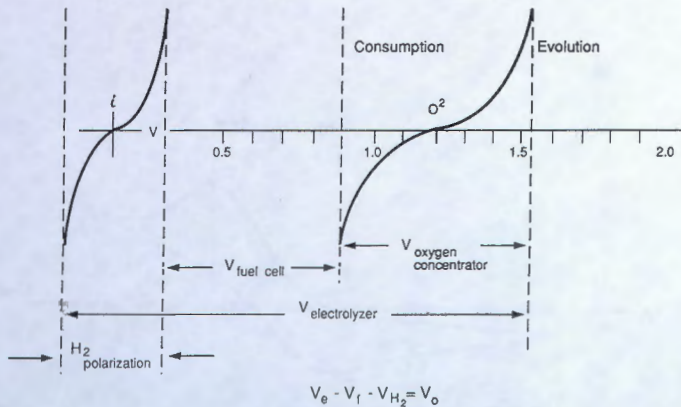


Figure 1. Estimation of electrolytic O₂ concentrator cell voltage

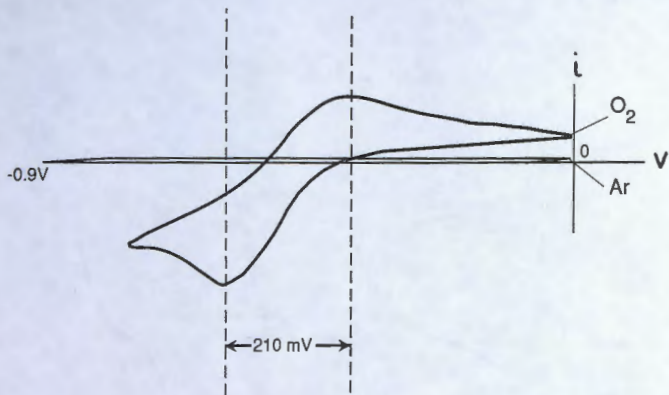


Figure 2. Current-voltage curve showing electrolysis of O_2 in aprotic organic solvent.