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Use of a Hydrogen Anode for Nitrate Waste Destruction

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ABSTRACT

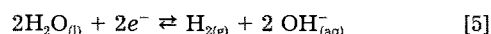
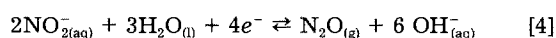
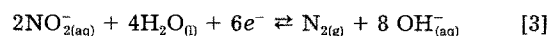
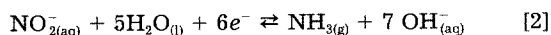
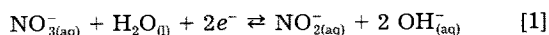
The use of a hydrogen gas-fed anode and an acid anolyte in an electrochemical cell used to destroy nitrate is demonstrated. A mixed $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$ anolyte is shown to favor nitrate cell performance and the generation of a higher hydroxide ion concentration in the catholyte. The suggested scheme is an apparent method of sodium sulfate disposal and a possible means through which ammonia (to ammonium sulfate, fertilizer) and hydrogen gas could be recycled through the anode side of the reactor. This could result in a substantial savings in the operation of a nitrate destruction cell.

Introduction

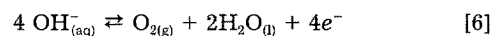
Large quantities of radioactive and hazardous wastes have been generated from nuclear materials production during the past fifty years. Processes are being evaluated to separate the high-level radioactive species from the waste and store them permanently in the form of durable solids. The schemes proposed will separate the high-level radioactive components, cesium-137 and strontium-90, into a small volume for incorporation into a glass waste-form. The remaining low-level radioactive waste contains species such as nitrites and nitrates that are capable of contaminating ground water. Electrochemical destruction of the nitrate and nitrite before permanent storage has been proposed.^{1,2} Not only will electrochemical processing destroy these species, the volume of waste could also be reduced.

Li *et al.*³ studied the electrochemical reduction of nitrate at nickel, zinc, lead, and iron cathodes in alkaline solutions. They found that nitrite was an intermediate in the electrochemical reduction of nitrate and that a lead electrode appears to be the best cathode for the reduction process. Hobbs *et al.*² reached the same conclusion with the effective treatment of both simulated and real wastes in a parallel-plate cell. Unfortunately, long-term use of lead electrodes is not environmentally acceptable. Using concentrated NaOH solutions with platinum and nickel electrodes, Li *et al.*⁴ found that generation of ammonia or nitrogen is highly dependent on applied current density. At lower current densities (less than 100 mA/cm²), nitrogen was the major gaseous product, while at higher current densities (460 mA/cm²) ammonia was the major product. Nickel appears to be the best choice of cathode material for the nitrate reduction process.

Nitrate/nitrite cell reactions.—In an alkaline solution at a lead or nickel electrode, the important cathodic reactions involving nitrogenous species are believed to be¹



The main reaction at the anode in a separated cell is the evolution of oxygen, as shown in Eq. 6. In an undivided cell, the nitrite species are reoxidized at the anode



The overall cell reaction shows that for every mole of nitrate or nitrite destroyed, one mole of hydroxide ion is produced.

Because ammonia gas is considered hazardous, the reduction of nitrate/nitrite to nitrogen gas is highly preferred. Unfortunately, the operating current required to achieve an economic reduction of nitrate (with respect to processing time) results in the generation of ammonia. Also, the oxygen generated at the anode (Eq. 6) can combine with ammonia, in the absence of a separator, to form an explosive mixture. The anodic evolution of oxygen gas consumes a high amount of energy. It is of interest, therefore, to reduce the energy required to operate a nitrate cell to an economically useful current density. With a hydrogen anode, the high energy consumption associated with oxygen evolution can be avoided and the hydrogen generated at the cathode returned to the anode for use.

A hydrogen anode can be used in an anolyte of sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), or a mixture of $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$. An anolyte of sulfuric acid or a mixture of sodium sulfate and sulfuric acid can be beneficial to a nitrate cell equipped with a hydrogen-consuming gas anode, because the ammonia produced on the cathode can be recycled by exposure to the sulfuric acid in the anolyte to produce ammonium sulfate (a fertilizer).

There is also an interest in the recovery of sodium hydroxide from sodium sulfate. Sodium sulfate (Na_2SO_4) is a by-product of sulfuric acid neutralization of alkaline process wastewater. One method of recovery of NaOH from sulfate waste, involves an electrochemical splitting of sodium sulfate in a membrane cell. In the splitting process, Na^+ ions from the Na_2SO_4 anolyte migrate into the cathode to combine with OH^- that is formed from H_2O reduction. Oxygen is generated on the anode. For the nitrate destruc-

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tion process, use of an acid sodium sulfate anolyte is attractive because of the possible formation of a more concentrated alkaline solution in the catholyte. A high hydroxide concentration does not favor hydrogen gas generation due to inefficient use of current in the nitrate cell. The formation of NaOH is encouraged by the migration of sodium ions from the anolyte. The alternative use of pure sulfuric acid as anolyte promotes the formation of a very dilute NaOH on the catholyte side, since the migrating protons from the anode side will primarily be used in the neutralization of the hydroxide ions formed in the catholyte. This favors hydrogen gas generation. Thus, in the proposed use of an acid sodium sulfate anolyte for the nitrate reduction process, the current efficiency for the formation of sodium hydroxide in the catholyte will depend on the ratio of protons [H^+] to sodium ions [Na^+] in the anolyte. Because the effective transport number of Na^+ ions and H^+ ions in Nafion is about 2:1,⁵ Na^+ ions will be transported into the catholyte from the anolyte more expediently.

Although a hydrogen-consuming anode can be employed in an alkaline environment, the commercially available acid-based hydrogen gas diffusion electrodes show superior performance over those used in alkaline solutions. This is an important reason for the evaluation of both acid- and alkaline-based hydrogen anodes in this work. An alkaline hydrogen anode is justified on the basis of cost since the catholyte (alkaline) product could, after purification, be reused on the anode side and thus eliminate the use of fresh NaOH anolyte. On the other hand, use of sulfuric acid or a sodium sulfate/sulfuric acid mixture as an anolyte could involve an added cost for the nitrate processing. However, since sodium sulfate is a readily available waste and its disposal into the environment is under strict control, it could be readily obtained at minimal cost.

The purpose of this paper is to report the preliminary results of the evaluation of a nitrate cell using a hydrogen-consuming anode in both alkaline and acid media. We intend to demonstrate the feasibility of an acid-based anolyte in the nitrate destruction cell. The use of a mixture of sodium sulfate and sulfuric acid (mixed anolyte) in a nitrate cell has not been demonstrated before.

Experimental

A bench-scale multipurpose continuous flow electrochemical reactor, capable of being configured either in a parallel-plate electrode mode or gas diffusion electrode mode, was used. The reactor was manufactured by Electrocell Co. (MPCell, Akersberga, Sweden). The electrode-to-separator gap (ion exchange Nafion® membrane) and the cross-sectional area are 0.7 cm and 7.0 cm², respectively. Each electrode has a macroscopic active surface area of 100 cm². In our present work, a nickel electrode 3.0 mm thick (Aldrich Chemical Co., Inc., Milwaukee, Wisconsin) was used as the cathode in all the runs. Run as a parallel-plate cell, a nickel electrode was used as the anode. In the gas diffusion mode, the anode consisted of a hydrogen-consuming anode supplied by E-Tek Inc. (Cleveland, OH) for the acid-based anolyte. An Alupower (New Jersey) supplied gas diffusion electrode was used in the alkaline anolyte. It is believed that platinum is the catalyst for both electrodes.

A schematic diagram of the equipment used is shown in Fig. 1. The flow circuit includes recycled anolyte and catholyte loops. A metered flow of catholyte was recycled through the cathode from a 5.0 liter tank. The reactor was not cooled. A water-cooled condenser was mounted at the top of each tank to condense vapor carried over by the disengaged gaseous products from the reactor. Gilmont flowmeters with manually controlled valves measured the anolyte and catholyte flows. The catholyte flow rate was held at a constant rate of 3.8 liter/min. A regulated dc power supply with a maximum power output of 1.8 kVA and capable of controlling either voltage up to 60.0 V or current up to 30 A was used. All parts in contact with the electrolytes were made of polypropylene. Laboratory-

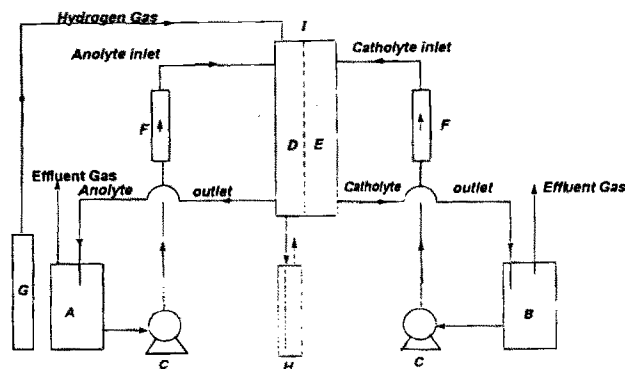


Fig. 1. Schematic diagram of the nitrate cell flow system: (A) anolyte reservoir, (B) catholyte reservoir, (C) pump, (D) anode chamber of multipurpose cell, (E) cathode chamber of multipurpose cell, (F) flowmeter, (G) hydrogen gas tank, (H) water column for hydrogen overpressure, and (I) multipurpose cell.

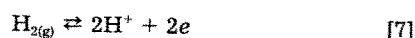
grade chemicals were used in deionized water. Hydrogen was of greater than 99.9% purity. In the diffusion anodes, the hydrogen supply into the anode was maintained at a constant flow rate of 30 cm³/min at an overpressure of 36.8 kPa.

The major independent variables were the superficial operating current densities (100 to 250 mA/cm²) and anolyte type (H₂SO₄, Na₂SO₄, NaOH). The concentration of pure sulfuric acid anolyte was between 1.5 and 1.6 M. For a mixed anolyte, H₂SO₄ and Na₂SO₄ concentration were 0.95 and 1.6 M, respectively. For a pure NaOH anolyte, the anolyte concentration varied between 1.6 and 6.1 M. In all the experiments in which sodium sulfate was used as an anolyte, changes in the anolyte Na^+ ion concentration with time were followed. The catholyte and anolyte were charged with known concentrations of their respective components (NaOH, NaNO₂, and NaNO₃ for the catholyte and H₂SO₄, or H₂SO₄ + Na₂SO₄, or NaOH for the anolyte). The concentrations of nitrate and nitrite were determined by ion chromatography, while atomic absorption spectroscopy was used for the Na^+ ions. The OH^- and H^+ were determined by titration. The cell voltage and applied current were measured by a voltmeter and an ammeter, respectively.

Results and Discussion

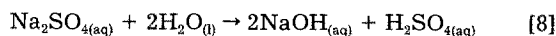
The nitrate and nitrite species are considered nonbenign in this process. The desired objective in the electroprocessing of the nitrate/nitrite solution is to totally reduce the nitrates and nitrites to nitrogen with a minimal formation of ammonia. Thus, a cell's performance could be expressed in terms of the fraction of unreacted nitrate/nitrite species. Equations 1 to 5 show that the reduction of these nonbenign species is a consecutive reaction process. In a membrane process such as this, water is transported across the membrane by electrosmotic and concentration differences. This results in variable volume processing. To account for this effect, the concept of "fraction of unreacted species per unit volume change," β_{pu} , is used (see Appendix). The concept was used as a criterion to determine the performance of a membrane cell in which electrosmotic water transport and consecutive species reactions occur. This criterion is useful when either the initial or final volume of the electrolyte in the recirculation tank is not known. In this work, the composition and identity of the gases formed on the cathode were not measured or determined.

For the proposed hydrogen gas consuming anode, the oxygen evolution reaction 6 will be replaced by hydrogen oxidation



Reaction 7 occurs both in pure sulfuric acid or mixed anolyte of sodium sulfate and sulfuric acid. However, in a mixed anolyte, Na^+ and H^+ ions are available for transport

across the membrane as current carriers. The overall reaction for a Na_2SO_4 anolyte is therefore represented by



This in effect translates to the splitting of sodium sulfate into sulfuric acid (anode side) and sodium hydroxide (cathode side). For all of the anolytes used, reactions 1 to 5 will take place on the cathode.

Figure 2 shows the fraction of unreacted nonbenign (nitrate and nitrite) species per unit volume change as a function of run time in NaOH - and acid-based hydrogen-consuming anodes. The current density is the superficial current density based on the macroscopic surface area of the electrode. In the figure, the overall combined concentrations of both nitrate and nitrite decrease with time. When the individual species are plotted as a function of time, the nitrate species concentration is observed to steadily decrease with time of run, while the concentration of the nitrite rises and falls for a time period as shown in Fig. 3. The increase in nitrite ion suggests that initially, the high concentration of nitrate favors its conversion to nitrite. As the nitrite level increased, the subsequent conversion of nitrite to either ammonia or nitrogen is favored. The result in Fig. 2 suggests that the hydrogen anode performance in acid anolyte is slightly better than its performance in alkaline. The advantage in acid is very small. The main reason for recommending an acid-based anolyte is the better control of hydrogen oxidation in acid media with commercially available gas diffusion electrodes.

The interaction between the concentration of the acid anolyte and the alkaline catholyte and its effect on cell performance is shown in Fig. 4. With a hydrogen gas-consuming anode, hydrogen is oxidized on the anode. The H_3O^+ formed in the process is transported across the membrane to the catholyte side where it interacts with OH^- ions to form water. Since there is competition between the reduction of water and the nonbenign species, the fraction of unreacted nonbenign species will be related to the $[\text{H}^+]/[\text{OH}^-]$ ratio where the H^+ and OH^- ions are measured in the anolyte and catholyte recirculating tanks, respectively. In Fig. 4, β_{pu} is plotted vs. the $[\text{H}^+]/[\text{OH}^-]$ ratio. From the figure, it is observed that the ratio decreases with current density, suggesting that production of H^+ was

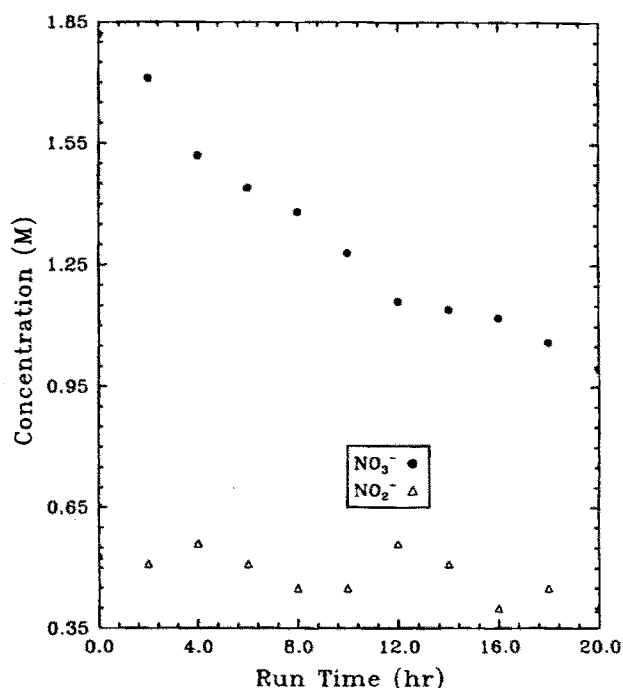


Fig. 3. Dependence of nitrate and nitrite species concentration on run time.

not keeping up with production of OH^- . The $[\text{H}^+]/[\text{OH}^-]$ ratio is important because the H^+ generation rate in the anolyte and its migration into the catholyte for subsequent neutralization of OH^- ions is controlled by the applied current density. At higher current densities, the high generation rate is offset by the high migration rate into the catholyte, which leads to low OH^- ion concentration. At 150 mA/cm^2 the rate of H^+ ion generation and migration is low. Similarly, the OH^- ion generation rate is also low. A plot of the nitrate/nitrite concentration vs. the $[\text{H}^+]/[\text{OH}^-]$ shows that the nitrate level increases with an increase in the $[\text{H}^+]/[\text{OH}^-]$ ratio.

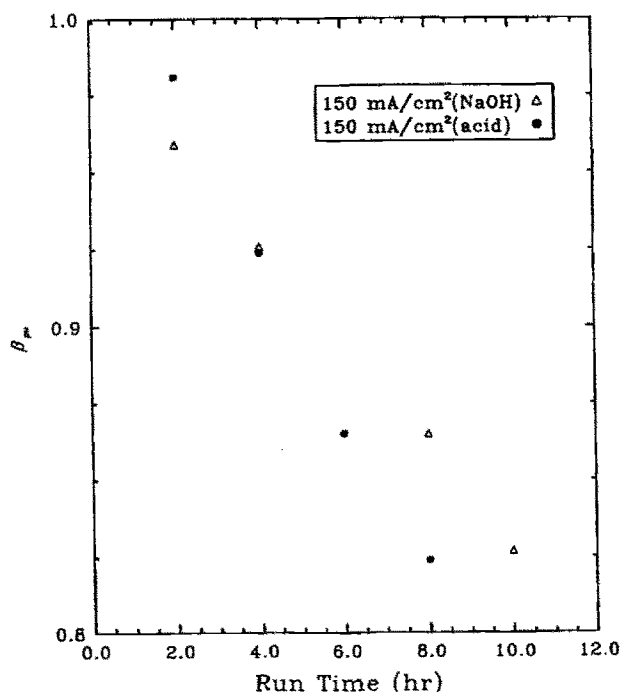


Fig. 2. Performance of hydrogen gas-consuming anodes in NaOH and H_2SO_4 anolytes.

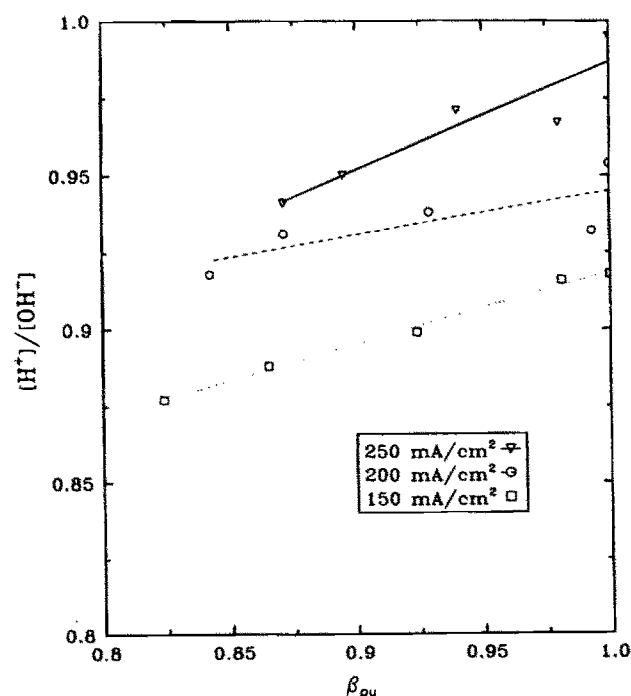


Fig. 4. Ratio of anolyte side H^+ to catholyte side OH^- ions vs. β_{pu} .

A comparison of the effects of sodium sulfate in the anolyte is shown in Fig. 5 to 7. As a result of the H^+ ion migration from the anolyte to the catholyte, the use of sulfuric acid as an anolyte limits the concentration level of OH^- ions generated in the cathode. When sulfuric acid is used as the anolyte, H^+ ions are the main current carrier across the membrane. The transported H^+ ions into the catholyte neutralizes the OH^- ions. In an Na_2SO_4/H_2SO_4 anolyte, protons and Na^+ ions compete as current carriers. Figure 5 compares the effects of pure sulfuric acid to a mixture of sulfuric acid and sodium sulfate. The x-axis in Fig. 5 represents the total energy required to reduce a unit mass of combined nitrate and nitrite at 50% conversion. The presence of sodium sulfate seems to favor the reduction process. The reason for this is not quite clear, except that with H^+ ion transport occurring in pure acid, a cyclical process of OH^- generation and neutralization could be occurring in the catholyte. This inefficient use of applied current means less destruction of nonbenign species. This is not the case when the Na^+ ion is part of the current carrier.

The effect of sodium sulfate on the catholyte side of the OH^- ion is shown in Fig. 6. With pure sulfuric acid, the OH^- ion level in the catholyte is limited to under 2.0 M after 10 h of running. However, with the use of sodium sulfate anolyte, the OH^- ion concentration in the catholyte rises faster than that obtained with a sulfuric acid anolyte. The merit of sodium sulfate lies in the higher transport number of Na^+ ions over H^+ in the Nafion® membrane. The concentration of OH^- ion in a cell utilizing H_2SO_4/Na_2SO_4 anolyte is dependent on the ratio of $[H^+]/[Na^+]$ in the anolyte. This is shown in Fig. 7. The curve approaches an optimum $[H^+]/[Na^+]$ ratio (~ 2.0) above which the concentration of NaOH seems to level off. If this maximum value is exceeded, the OH^- ion concentration starts to decrease. This is because the anolyte Na^+ ion concentration has decreased to a level that H^+ transport into the cathode side favors water formation and cyclical OH^- generation and neutralization. Thus, in a practical application, sodium sulfate makeup has to be continuously added to the anolyte to maintain an $[H^+]/[Na^+]$ ratio equal to or less than the optimal value. Since the OH^- ion competes with the nitrite and nitrate ions on the cathode for reaction, the anolyte side $[H^+]/[Na^+]$ ratio at which the catholyte OH^-

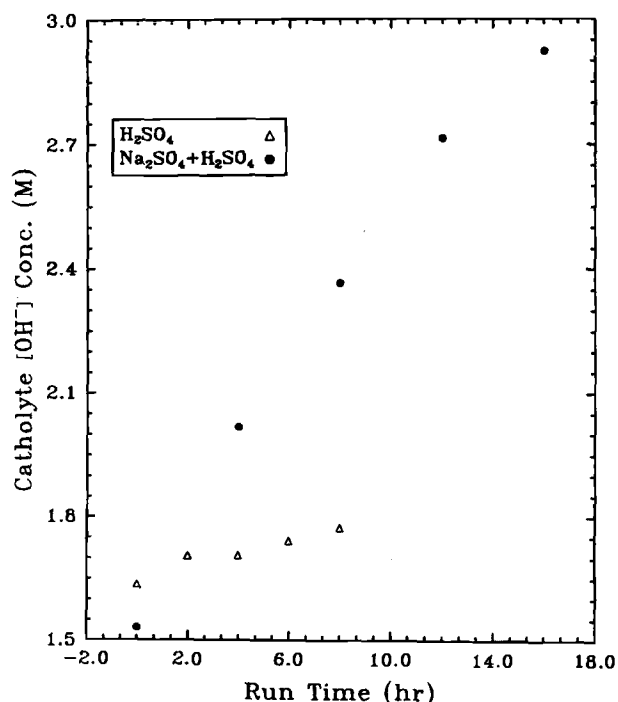


Fig. 6. Catholyte OH^- concentration with and without Na_2SO_4 anolyte.

concentration levels off may be used as a means of controlling the availability, and hence, the reactivity of OH^- ions on the cathode.

The performance of a parallel-plate (nickel anode) electrode is compared to a hydrogen gas-consuming anode at high current density in Fig. 8, while the cell voltage for these two systems are compared in Fig. 9. As pointed out earlier, at high current density, both high proton migration and OH^- ion neutralization leads to a cyclical process involving inefficient hydrogen gas generation on the cathode. Thus, the performance of the parallel-plate cell

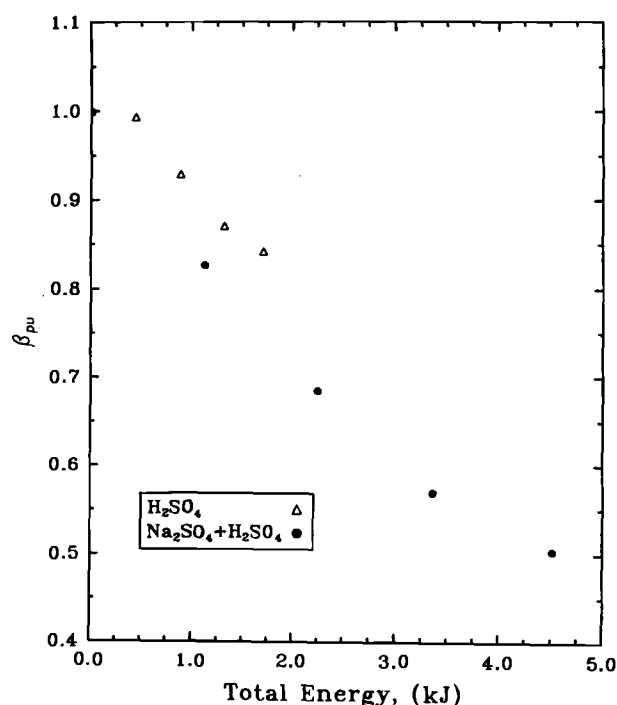


Fig. 5. Unreacted species, β_{pu} , with and without Na_2SO_4 at 200 mA/cm².

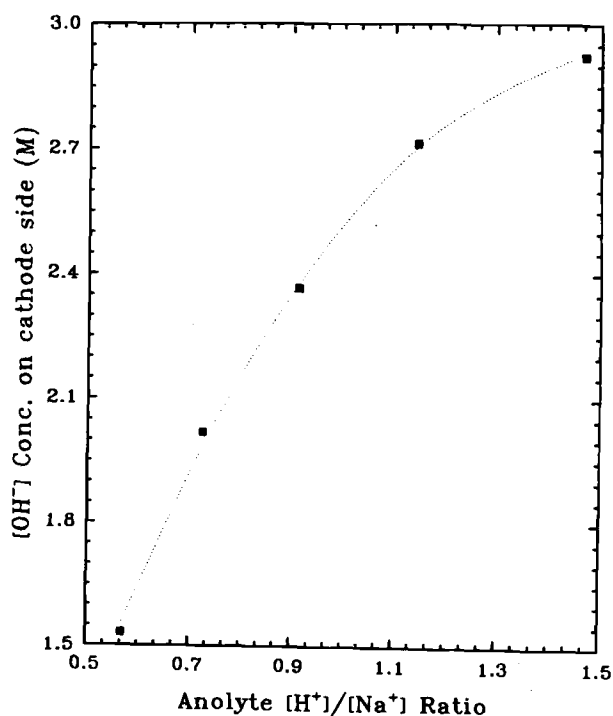


Fig. 7. Catholyte OH^- dependence on anolyte $[H^+]/[Na^+]$ ratio at 200 mA/cm².

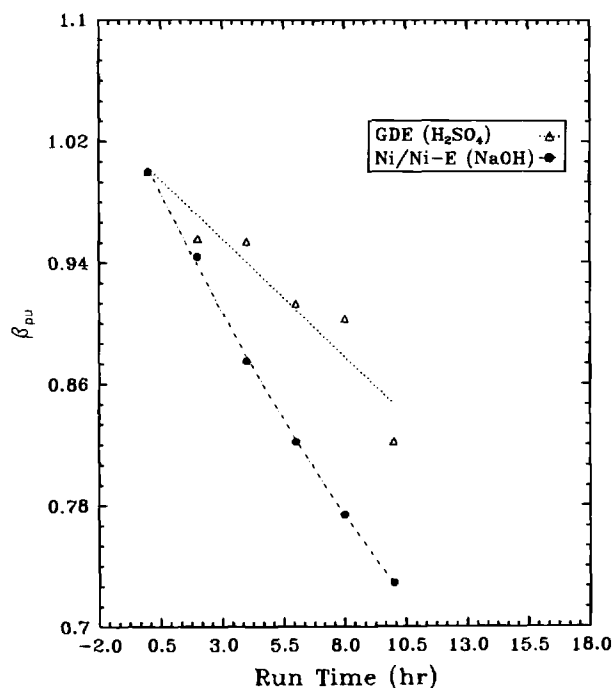


Fig. 8. Cell performance in NaOH anolyte [no gas diffusion electrode (GDE)] vs. acid anolyte with GDE at 250 mA/cm².

appears better than the performance obtained with a gas diffusion anode.

The variation of cell voltage with time at a constant current density is shown in Fig. 9. Compared to the results obtained in the absence of a gas diffusion electrode, a substantial voltage drop of about 0.4 to 1.8 V at 250 mA/cm² is observed. This translates to a substantial energy savings for the use of a hydrogen gas-consuming anode. The energy savings here may not translate into any substantial cost advantage when the costs of hydrogen gas and the hydrogen electrode are factored in. The high energy consumption of

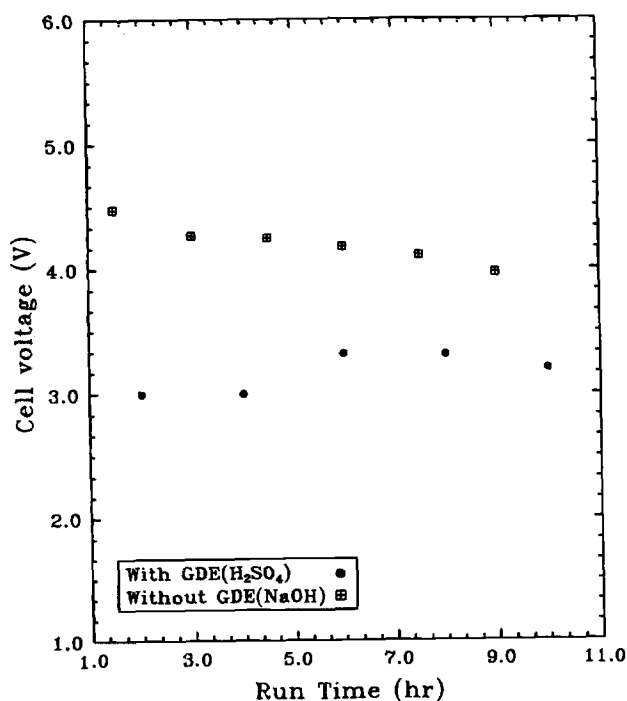


Fig. 9. Variation of cell voltage with and without gas electrode at 250 mA/cm².

the oxygen-generating step at the anode is due to the high overvoltage associated with oxygen evolution. It is conceivable that the required hydrogen in the anode could be reclaimed from that produced at the cathode in this process.

Conclusion

The feasibility of an acid-based anolyte in the nitrate destruction cell has been demonstrated. Further experiments are required to investigate the interaction of the key parameters (current density, flow rates, temperature, [H⁺], etc.) in the process. Splitting of acidic sodium sulfate is an attractive anolyte process for waste minimization. A further incentive for this process is the substantial energy savings resulting from the use of a gas diffusion electrode and possible recycling and treatment of generated ammonia. The use of an acid anolyte is not dependent on the use of a gas diffusion electrode. Thus, both sodium sulfate splitting and nitrate destruction could be carried out simultaneously with or without the use of a gas diffusion electrode.

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APPENDIX

The performance factor, "fraction of unreacted species/volume change," β_{pu} , derived below, is a dimensionless quantity and measures the sum total of unwanted species (pollutants) that are unreacted per unit volume change. It is a measure of the cell's "extent of performance for unreacted species" (β_{pu}) at the prevailing operating conditions. It is a conservative performance criteria for a cell involving osmotic water transport when the electrolyte tank volume change is not known. The β_{pu} value of a cell departs from the traditional fraction of unreacted species by the ratio of the initial electrolyte volume to the final volume after reaction (dilution ratio). A simple species balance at the start of a batch process gives the total amount of species to be destroyed as

$$F^o = \sum_{i=1}^n m_i c_i^o V^o \quad [A-1]$$

where, F^o (g) is the total mass of the species contained in an initial electrolyte volume, V^o (cm³) of the tank (anode or cathode side) of interest, and m_i and c_i^o are the formula weight and initial concentration of species, i , respectively. At the end of the batch processing time, t , the total electrolyte tank volume of interest changes. The change in this volume could either be an increase (water received) or a decrease (water loss). A species material balance yields

$$F_t = \sum_{i=1}^n m_i c_i V_t \quad [A-2]$$

where V_t is the electrolyte volume at time, t . Thus, the fractional change, γ , (in the amount of unreacted species) is obtained by dividing Eq. A-2 by Eq. A-1 as

$$\gamma = \frac{\left(\sum_{i=1}^n m_i c_i \right) V_t}{\left(\sum_{i=1}^n m_i c_i^o \right) V^o} = \frac{F_t}{F^o} \quad [A-3]$$

If we define β_{pu} as follows

$$\beta_{pu} = \frac{\left(\sum_{i=1}^n m_i c_i \right)}{\left(\sum_{i=1}^n m_i c_i^o \right)} \quad [A-4]$$

then Eq. A-3 could be rewritten as

$$\gamma = \beta_{pu} \frac{V_t}{V^o} \quad [A-5]$$

But the species extent of reaction, ϵ , is defined as

$$\epsilon = 1 - \gamma \quad [A-6]$$

By substituting for γ in A-6 using A-5 and solving for β_{pu} , we obtain

$$\beta_{pu} = (1 - \epsilon) \frac{V^o}{V_t} \quad [A-7]$$

Thus, β_{pu} will be equal to the traditional "fraction of unreacted species" ($1 - \epsilon$) when there is no volume change or dilution of initial electrolyte tank volume. Conceptually, β_{pu} is proportional to $(1 - \epsilon)$ where the constant of proportionality is the extent of dilution resulting from water transport. This performance criteria should not be confused with $(1 - \epsilon)$.

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The Performance and Stability of Ambient Temperature Molten Salts for Solar Cell Applications

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ABSTRACT

Room temperature molten salt systems based on methyl-hexyl-imidazolium iodide (MHImI) have been used to scrutinize the performance characteristics, the stability and the mass-transfer effects in a photoelectrochemical regenerative device, as the latter is influenced and can even be limited by local concentration and mass-transport of the electroactive redox mediator species in the electrolyte phase. These salts appear to afford particular advantages over organic liquids as solvents for solar cell electrolytes. Cell performance showed outstanding stability, with an estimated sensitizer turnover in excess of 50 million. An investigation has been carried out on the physical-electrochemical properties of MHImI and its mixtures with organic solvents such as n-methyl-oxazolidinone, acetonitrile and with other lower viscosity molten salts such as methyl-butyl-imidazolium triflate. The repercussions of these properties on solar cells is described experimentally by the performance of practical application devices. Simulation models of mass transport in the nanocrystalline solar cell help illustrate operational aspects such as concentration profiles, limiting currents, anticipated mass-transfer overpotential as a function of current density, and they help to make projections as to how the properties of molten salt electrolytes can be better exploited toward this practical end.

Introduction

Recently, many solar cells have been developed based on the regenerative photoelectrochemical principle.^{1,2} At this stage, an electrolyte based on salts dissolved in organic solvents is used. Such an electrolyte presents some drawbacks: (i) the volatility of the solvent implies that the construction of the cell must be absolutely tight; (ii) the solubility of the salts could be overstepped when the cell works at lower temperature than anticipated, resulting in precipitation; and (iii) solvents are often incompatible with the glues used to seal the cell. To avoid one or all these problems, other kinds of electrolyte can be used. One possibility is to use an ion-conductive solid, but in the case of solid junction, the quality of the interface is critical. This is one reason why electrolytes based on polymers were developed. The ability of the polyelectrolytes or polymer electrolytes to form films and the elasticity of the latter allow good interfaces to be obtained. In the case of a porous electrode, polyelectrolytes are, however, not convenient, as filling the pores is difficult. That is why we have reported our choice of electrolytes based on room temper-

ature molten salts which combine the advantages of solvent-based electrolytes and those of polyelectrolytes. The major drawback of such electrolytes is that they are confined to moderate power applications due to high viscosities of the salts.

The molten salts can play the role of solvent only,³ or be involved in the mediator electrochemical processes. A mixture of an electroactive molten salt with an electroinactive one which is less viscous seems to be the right compromise. Some research is being done in our group to identify room temperature molten salts with very low viscosities.⁴

Molten salts are ionic liquids and as such can be utilized in a wide range of electrochemical applications where high conductivity and ionic mobility are required. Their ionic nature renders them negligibly volatile in the liquid state. These properties as well as relatively low viscosity, the large electrochemical window, thermal stability, miscibility with solvents or other salts and hydrophobicity are a few of the desirable qualities found in certain molten salts synthesized in our group⁴ and reported by others,⁵ making them attractive for use as electrolytes and solvents in the dye-sensitized nanocrystalline solar cell. The methyl-hexyl-imidazolium iodide (MHImI) has been found, thus far, to be the least viscous iodide molten at room temperature, not sensitive to water, and stable under the operational conditions of the dye-sensitized, nanocrystalline

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