Reports

Energy Recovery from Saline Water by Means of Electrochemical Cells

Abstract. *An electrochemical concentration cell is proposed as a means of extracting the energy released from the mixing of freshwater with seawater. In order to obtain the maximum power from such a cell, a small amount of seawater must be added to the freshwater prior to its introduction into the cell in order to lower the internal resistance of the cell. The work available from the electrochemical concentration cell is of the same order of magnitude as the work derived from the use of an osmotic pump to extract energy from seawater. Both of these saline water techniques should be considered when unconventional, long-range power sources are evaluated.*

Several recent publications have dealt with the possibility of extracting the energy released from the mixing of freshwater with seawater (*1, 2*). In all of these approaches an osmotic pump of some type has been used, and at present these techniques probably are of more theoretical interest than practical value. Nevertheless, they do constitute possible energy sources that should be evaluated.

We consider here a different approach to extracting the energy from the mixing of freshwater with seawater, one that involves the direct generation of electricity via an electrochemical concentration cell. Earlier saline water techniques involved the development of hydrostatic pressure with subsequent conversion to mechanical energy and then the generation of electrical energy.

Electrochemical concentration cells (*3*, pp. 544–551) can be schematically illustrated as in Fig. 1. Imagine that side A is filled with freshwater and side B with seawater. The electrodes in both compartments are reversible chloride electrodes, and a porous plug (y) separates the two sides of the electrochemical cell. The electromotive force (emf) of such a cell can be calculated from Eq. 1 (*3*, p. 551):

$$\text{emf} = 2t_{\text{Na}}\frac{RT}{F}\,\ell\text{n}\left(\frac{C_A\,\gamma_A}{C_B\,\gamma_B}\right) \qquad (1)$$

where t_{Na} is the transference number of Na^+, R is the gas constant, T is the absolute temperature, F is the Faraday constant, C_A and C_B are the respective concentration of Cl^- in sides A and B of the cell, and γ_A and γ_B are the respective mean molal ionic activity coefficients. For seawater C_B = 0.5 molal, whereas for Mississippi River water (*4*) $C_A = 4.2 \times 10^{-4}$ molal [15 parts per million (ppm)]. Substituting these values along with standard physical chemical values for the other quantities in Eq. 1, we obtain

$$\text{emf} = 2 \times 0.3\,\frac{8.3 \times 300}{96{,}500} \times \ell\text{n}\,\frac{0.5 \times 0.68}{(4.2 \times 10^{-4})\,(1)} = 0.1 \text{ volt} \qquad (2)$$

This concentration cell may not be the "best" one that can be obtained from these water sources. This cell would have a high internal resistance, and to lower the internal resistance it might be desirable to mix some of the seawater with freshwater prior to introduction into the electrochemical cell. It thus becomes important to determine the concentration of salt (NaCl) that should be present in the freshwater side of the cell in order to obtain maximum power.

The power P that can be derived from electrical circuits involving electrochemical cells can be represented as

$$P = \frac{\epsilon^2}{R_{i+e}} \qquad (3)$$

where ϵ is the cell emf, and R_{i+e} is the combined internal and external resistance of the circuit. For maximum power $P_{\max}$ the internal resistance R_i equals the external resistance R_e (*5*); therefore, Eq. 3 becomes

$$P_{\max} = \frac{\epsilon^2}{2\,R_i} \qquad (4)$$

If we assume that γ_A is unity, Eq. 1 may be written as

$$\text{emf} = \frac{2 \times 0.3 \times 8.3 \times 300}{96{,}500} \times \left[\ell\text{n}\,(0.5 \times 0.68) - \ell\text{n}\,C_A\right] \qquad (5)$$

or

$$\text{emf} = -0.0155\,(1.08 + \ell\text{n}\,C_A) \qquad (6)$$

The specific resistance of the dilute electrolytic solution is the reciprocal of the conductance of the solution. Standard physical chemical equations (*3*, pp. 443–451) concerning conductance can be combined to give

$$R_c = \frac{1000K}{C_A\,(\Lambda_0 - b\,C_A{}^{1/2})} \qquad (7)$$

where R_c is the cell resistance, K is the cell constant, C_A is the NaCl concentration in the freshwater side, Λ_0 is the equivalent conductance at infinite dilution, and b is the Onsager slope constant. If we assume that for the cell depicted in Fig. 1 R_i is mainly the electrical resistance of the freshwater side, then Eqs. 4, 6, and 7 may be combined to yield

$$P_{\max} = \frac{(-0.0155)^2(1.08 + \ell\text{n}\,C_A)^2 C_A(\Lambda_0 - b\,C_A{}^{1/2})}{2(1000K)} \qquad (8)$$

Handbook values for Λ_0 and b for NaCl solution may be substituted in Eq. 8 to give

$$P_{\max} = K'\,C_A(1.08 + \ell\text{n}\,C_A)^2 \times (126.45 - 79.4\,C_A{}^{1/2}) \qquad (9)$$

where K' is a constant.

If we differentiate Eq. 9 with respect to concentration and set the derivative equal to zero, we obtain

$$0 = 2\,(126.45 - 79.4\,C_A{}^{1/2}) + (1.08 + \ell\text{n}\,C_A) \times (126.45 - 79.4\,C_A{}^{1/2}) - 39.7\,C_A{}^{1/2}\,(1.08 + \ell\text{n}\,C_A) \qquad (10)$$

Equation 10 may be easily evaluated on a computer to yield C_A = 0.039 molal (2300 ppm of NaCl). This is the concentration of NaCl needed in side A of Fig. 1 to yield the maximum power. As this NaCl concentration is considerably above that of most river water, it will be necessary to mix some seawater with the freshwater prior to introduction into the electrochemical concentration cell. The emf to be expected from the cell, calculated from Eq. 5, is 0.035 volt.

Concentration cells are usually constructed in electrochemistry laboratory experiments to determine transport numbers and other quantities of theoretical interest. Their use as a power source (even on a small scale) has not been investigated. However, a NaCl concentration cell of the type proposed probably is a good one to consider as a power source because (i) it is the usual cell that is constructed in the laboratory and (ii) commercial reversible chloride electrodes have been developed for chlorine production.

It is difficult to compare the osmotic pump or the electrochemical concentration cell as preferred methods of extracting the energy released from the mixing of freshwater and saltwater. One can compare the maximum work that is possible in the two processes. Norman has calculated (*1*) the work W that can be derived from a saline water osmotic pump:

$$W = \frac{RTC}{V} \qquad (11)$$

where C is the concentration of the seawater and V is the volume of water. If one considers the energy to be derived from the addition of 1 liter of freshwater to an infinite amount of seawater, then from (*1*)

$$W = \frac{2 \times 300 \times 1}{1} = 600 \text{ cal}$$

For an electrochemical cell, the free energy or W_{max} that can be obtained is

$$W_{\text{max}} = n\, F\, \epsilon \qquad (12)$$

where n is the number of equivalents reacting. For a NaCl concentration cell, n equals 1 equivalent per mole of Cl^-. Calculating the energy released when the ions in 1 liter of seawater are transferred to freshwater, one obtains for the electrochemical concentration cell that has been maximized for power generation

$$W = 0.5 \times 23{,}000 \times 0.035 = 400 \text{ cal} \qquad (13)$$

This available work is of the same order of magnitude as that obtained by the osmotic pump, and the generation of electricity by direct means rather than by means of a three-step process has some advantage. The agreement between the calculated W_{max} in the two processes is not surprising, since these are two ways of deriving energy from the same energy source.

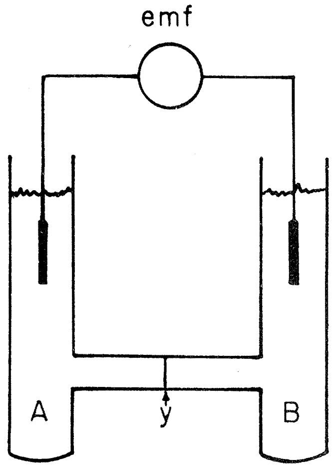

Fig. 1. Electrochemical concentration cell.

There are, however, conceptual differences between the two approaches: in the osmotic pump, water molecules are transported across a membrane; in the electrochemical concentration cell, ions are transported across a membrane. In an interesting practical approach to the use of saline water electrochemical concentration cells as power sources (*6*), ion-exchange membranes have been used to separate the anode and cathode compartments; by this means, one of the most difficult practical problems associated with electrochemical concentration cells has been solved.

Perhaps the biggest obstacle to the use of saline water as an energy source is that the energy-rich phase (that is, the seawater) is in plenteous supply; whereas the energy-poor phase (that is, the freshwater) is in limited supply. Therefore, saline water power plants employing electrochemical concentration cells would need to be located near where rivers enter into the sea or perhaps even in Arctic waters where freshwater could be obtained from the ice.

Another approach would be to use highly saline lakes (for example, the Dead Sea) as the energy-rich phase and seawater as the energy-poor phase. This approach would lead to higher power outputs per electrochemical concentration cell if suitable geographic locations can be found for such installations. It might be feasible to create artificial lakes near the ocean and use solar evaporation to increase their salinity so that energy dissipation can be achieved from the dilution of the saline lake water with seawater.

The sea is being seriously considered as an energy source (*7*). Most of the interest appears to be centered on the use of the thermal gradients in the ocean to generate electric power. On the basis of the evidence presented here, we believe that saline water electrochemical concentration cells and osmotic pumps should be seriously considered as potential long-range power sources.

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References and Notes

1. R. S. Norman, *Science* **186**, 350 (1974).
2. O. Levenspiel and N. de Nevers, *ibid.* **183**, 157 (1974); H. P. Gregor, *ibid.* **185**, 101 (1974); O. Levenspiel and N. de Nevers, *ibid.*, p. 102.
3. S. H. Maron and C. F. Prutton, *Principles of Physical Chemistry* (Macmillan, New York, 1959).
4. A. A. Levinson, *Introduction to Exploration Geochemistry* (Applied Publishing, Calgary, Alberta, Canada, 1974), p. 171.
5. C. E. Mendenhall, A. S. Eve, D. A. Keys, R. M. Sutton, *College Physics* (Heath, Boston, 1944), p. 429.
6. J. N. Weinstein and F. B. Leitz, *Science* **191**, 557 (1976).
7. R. J. Seltzer, *Chem. Eng. News* **54**, 19 (1976).
8. We thank H. K. Stryker for the computer computations.

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Extended Helical Conformation Newly Observed in Protein Folding

Abstract. *A new secondary structure, which shows regularity within the experimental error, is noticed in* α*-chymotrypsin, and considering its extended nature, the name* ε*-helix has been suggested for the same. The average observed values of* ϕ *and* ψ *for this conformation are* $-93°$ *and* $+146°$*, respectively. The helical parameters turn out to be* $n = -2.7$ *and* $h = 3.3$ *angstroms.*

During the course of an analysis of the crystallographic structural data of some proteins, which was performed by methods reported recently (*1*), we observed what appears to be a new regular form of secondary structure that apparently has not yet been described. We now report evidence for, and the nature of, this form of chain folding.

The observed overall frequency distribution of θ, which is the torsion angle involving the virtual bonds, namely, $C^{\alpha}_{(i-1)}$—$C^{\alpha}_{(i)}$—$C^{\alpha}_{(i+1)}$—$C^{\alpha}_{(i+2)}$, in six proteins (myoglobin, lysozyme, α-chymotrypsin, carboxypeptidase A, ribonuclease S, and insulin) containing, in all, about 1050 residues is shown in Fig. 1. It may be seen that there is a prominent maximum at $\theta \simeq 50°$, which corresponds to α helices. Apart from this there are two broad maxima, one at $\theta \simeq -135°$ and another at $\theta \simeq -170°$ (*2*).