Reports

Electric Power from Differences in Salinity: The Dialytic Battery

Abstract. *An array of alternating anion and cation exchange membranes can be used to generate electric power from the free energy of mixing of river and sea waters. A simple mathematical model, which predicts experimental results well, is useful in exploring conditions for optimization of the process. Major, but not impossible, improvements in technology would be required to bring the cost of power from the dialytic battery into line with foreseeable energy prices.*

The gravitational potential energy of river water provided our first major source of electricity, but fossil fuels now account for most of the electric power in the United States, even though hydroelectric power production has continued to increase. As fuel supplies are depleted, however, and as the future of nuclear power becomes less certain, we come full circle to river water as a geophysical energy option. Few good hydroelectric sites remain unexploited in this country, but a river flowing into the sea carries a second form of potential energy, a physical chemical energy, in its low salt content.

The "salinity potential" is about 20 atmospheres, equivalent to the hydrostatic head of a 700-foot (213-m) dam (*1*). Dilution of 1 m^3 of fresh water per second in a large volume of sea water dissipates approximately 2.25 Mw of power (*2*), some portion of which should be recoverable. The total world river flow of 1.08×10^6 m^3/sec (*3*) thus constitutes a renewable energy source of a theoretical 2.43×10^{12} watts. For comparison, the average rate of electric power generation in the world in 1973 was 0.69×10^{12} watts (*4*). A hypothetical device for capturing such free energy of mixing through the medium of hydrostatic pressure was recently presented in these pages (*5*). The same energy yield is theoretically available regardless of the method of conversion.

A simpler, more direct approach is the device which we shall refer to as a dialytic battery, shown in Fig. 1. Alternating anion and cation exchange membranes separate compartments through which pass solutions of two different salt concentrations. Metal electrodes in the two end compartments are connected through an external load to which power is delivered. Diffusive flows of sodium across each cation exchange membrane and of chloride across each anion exchange membrane establish a flux of electric charge between electrodes. The battery may take any of several geometric forms as long as the essential topology of the series array is maintained. Its operation is a reversal of conventional electrodialysis desalination, a process using the same kind of membrane stack, but with electric power as *input* and a difference in salinity as *output*.

Virtually every "new" idea actually has a long history, and the dialytic battery is no exception. In the early 1950's Manecke (*6*) experimented with an array of three membranes and analyzed such stacks for use as storage batteries (*7*). Pattle (*1*) constructed a membrane stack and obtained 0.015 watt from it by operating at an elevated temperature. This early work has not been followed up, and no one has previously examined the conditions for optimum performance of a dialytic battery or its potential for large-scale energy conversion.

In its simplest form our model assumes (i) that the feed solutions are of pure NaCl, (ii) that water flow through the membranes can be neglected, (iii) that concentration polarization near the membrane-solution interfaces is negligible, and (iv) that feed solutions do not change concentration appreciably along the channels. Each of these constraints can be relaxed, leading to more complex but still manageable mathematics (*8*). In the following discussion, we focus on systems using river and sea water, but highly saline bodies such as the Dead Sea offer more concentrated, although smaller, sources of salinity power (*9*).

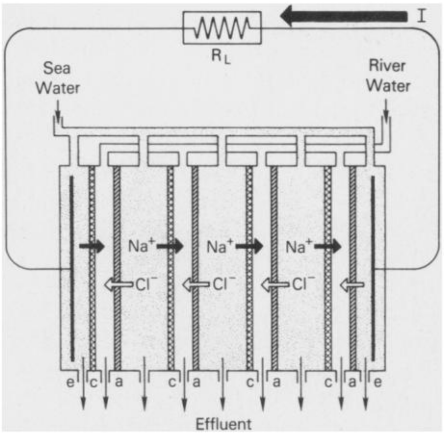


Fig. 1. A dialytic battery. The letters *e*, *c*, and *a* denote electrode, cation exchange membrane, and anion exchange membrane, respectively; R_L is the load resistance. In practice a stack would incorporate a large number of membranes, and the electrode compartments might be perfused separately.

A stack of *N* membrane pairs develops an open-circuit potential equal to the sum of the individual membrane potentials

$$V^{\circ}_{\text{stack}} = 2N \frac{\alpha RT}{\mathcal{F}} \ln(a_s/a_r) \qquad (1)$$

where *R* is the gas constant; *T* the absolute temperature; $\mathcal{F}$ the Faraday; *a* the NaCl activity; superscript o indicates open-circuit conditions; r and s denote the river and sea water compartments, respectively; and α expresses the average permselectivity of the membrane pair (*10*). For optimal performance α should be as near unity as possible, all else being equal.

The resistance (ohms) of the stack is the sum of the resistances of its series elements

$$R_{\text{stack}} = \frac{N}{A} \left(\mathcal{R}_a + \mathcal{R}_c + \mathcal{R}_r + \mathcal{R}_s\right) \qquad (2)$$

where *A* is the current-passing area of each membrane; the $\mathcal{R}$'s are area resistances (ohm cm^2); and a and c denote anion and cation exchange membranes, respectively. Assuming the thickness (*h*) of river and sea water compartments to be comparable within an order of magnitude, $\mathcal{R}_s$ will be small compared with $\mathcal{R}_r$, and

$$R_{\text{stack}} \approx \frac{N}{A} \left(\mathcal{R}_a + \mathcal{R}_c + \frac{h_r}{\Lambda_r c_r}\right) \qquad (3)$$

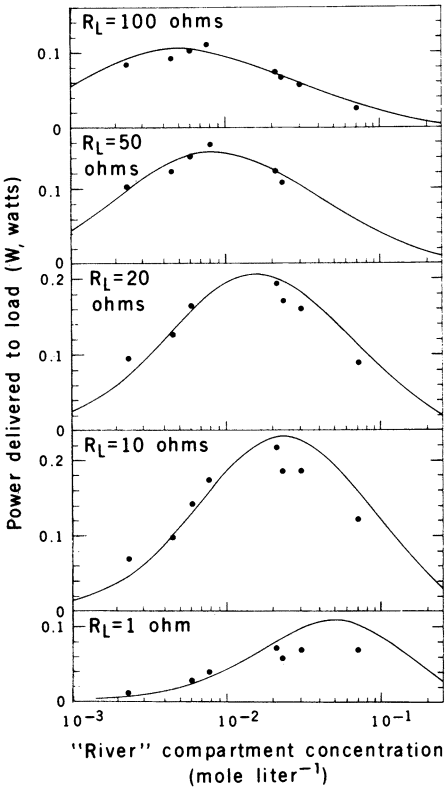
where Λ is equivalent conductance, and c_r is river water concentration. Electric current (*I*) in the load resistance (R_L) is found from Kirchhoff's law to be $V^{\circ}_{\text{stack}}/(R_{\text{stack}} + R_L)$. Additional terms reflecting the potential difference and resistance at each metal electrode are omitted since a large-scale apparatus would contain enough membranes to render electrode effects negligible (*11*). Finally, power delivered to the load is given by an expression formally identical to that for any battery

$$W = I^2 R_L = \frac{(V^{\circ}_{\text{stack}})^2 R_L}{(R_{\text{stack}} + R_L)^2} \qquad (4)$$

Equation 4, with insertion of values from Eqs. 1 and 3, predicts the power output of the dialytic battery as a function of the transport properties of its individual elements.

To test the model, we converted an electrodialysis stack into a dialytic battery by changing the external electric circuit and operating conditions. In Fig. 2 the theoretical predictions of Eq. 4 are compared with power outputs actually obtained at various "river water" concentrations and resistive loads, using a "sea water" consisting of 0.57*M* NaCl.

Optimal operating conditions for such a stack will be determined by a variety of en-



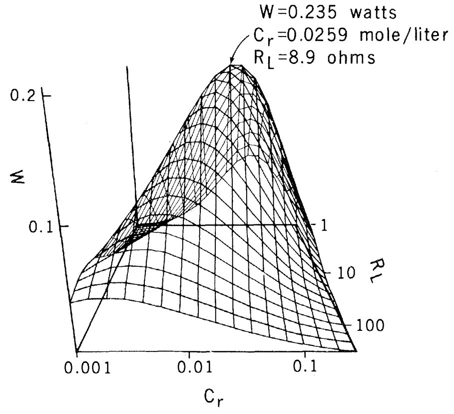


Fig. 2 (left). Power output of the dialytic battery as a function of "river water" concentration and load resistance (R_L). The stack contained 30 anion and 31 cation exchange membranes (103QZL and 61CZL from Ionics, Inc.). Solution compartments of both types were 1 mm thick and contained turbulence promoters. Solution velocities were 15 cm/sec, high enough to avoid significant polarization. An ammeter in the external circuit recorded electric current, and stack voltage was measured between neutral electrodes inserted in the last membrane at each end of the stack. Since this prototype contained a relatively small number of membranes, a d-c power source was placed in the circuit to compensate for energy consumption at the electrodes. Theoretical curves are from Eq. 4, with the following parameters taken from separate measurements or from the literature (*17*): $\mathcal{R}_a = \mathcal{R}_c = 11$ ohm cm^2, $\alpha = 0.64$, $h_r = 0.1$ cm, $\Lambda_r = 0.0961$ liter ohm^{-1} mole^{-1} cm^{-1} (20°C), $a_s/a_r = (c_s/c_r)^{0.917}$, $N = 30$, $A = 232$ cm^2, and $c_s = 0.57M$. Fig. 3 (right). Contour plot of power expected from the dialytic battery according to Eq. 4. Parameter values are listed in the legend to Fig. 2. The optimum power (0.235 watt) is obtained with $c_r = 0.0259$ mole liter^{-1} and $R_L = 8.9$ ohms.

gineering and economic considerations. If, for instance, availability of fresh water were the limiting factor, the process should be run very slowly ($R_L \gg R_{\text{stack}}$) and the river water used until its salt concentration approached that of sea water. If, on the other hand, capital costs were dominant (as seems probable), energy output per unit time should be maximized by establishing the impedance-matched condition $R_L = R_{\text{stack}}$, in which case

$$W = AN \frac{[(\alpha RT/\mathcal{F})\ln(a_s/a_r)]^2}{\mathcal{R}_a + \mathcal{R}_c + h_r/\Lambda_r c_r} \quad (5)$$

The power output per unit area is simply W/AN.

Equation 5 indicates an interesting relationship between power output and river water concentration under impedance-matched conditions. A decrease in river water concentration tends to improve performance by increasing the potential difference across each membrane but degrades performance by increasing resistance in each dilute compartment. Differentiation of Eq. 5 leads to an implicit expression for that value of c_r which balances these effects and maximizes power output:

$$\ln\left(\frac{c_s}{c_r}\right)_{\text{optimum}} = \frac{2(\mathcal{R}_a + \mathcal{R}_c + \mathcal{R}_r)}{\mathcal{R}_r} \quad (6)$$

where $\mathcal{R}_r$ is considered inversely proportional to c_r, and the activity ratio is related to the concentration ratio as noted in the legend to Fig. 2. For our stack and experimental conditions the optimum value of c_r is $0.0259M$, so power output would tend to increase initially if river water (usually 0.005 to $0.015M$) became progressively more saline as it flowed down each channel. The optimum with respect to R_L and c_r is shown in Fig. 3.

Optimization of other parameters involves a more complex set of trade-offs. For example, Eq. 5 indicates that large increases in power per unit membrane area are most likely to be achieved by decreasing membrane resistance and river compartment thickness, but those changes can be pushed only so far. The decrease in thickness would increase the cost of pumping water through the stack at a specified velocity (even though less water need be pumped) and would also necessitate higher flow velocities to reduce concentration polarization resulting from the higher current densities. A more extensive analysis of the process should take into account polarization, transmembrane water flux, fractional use of the salinity potential, pumping requirements, and pretreatment of the water to reduce membrane fouling.

As a society we have not decided how much we are willing to pay for such intangible benefits as the avoidance of fission hazards, the elimination of various pollutants, and the conservation of remaining fossil reserves. In the long run, such considerations may be more important than price per se, but it is necessary, as with all new energy sources, to ask whether the dialytic battery can produce power at a reasonable cost. The following extrapolation from the performance of our prototype, assuming major improvements in technology but no fundamental breakthroughs, may put the challenge in better perspective.

Membranes of the same materials as those in our battery but one-tenth as thick (0.06 mm) have been made and their transport properties determined (*12*). If these were incorporated into a stack with river water compartments 0.1 mm thick, the projected optimum output would be 1.7 watt/m^2, a tenfold improvement over our experimental results (*13*). Standard electrodialysis membranes currently cost on the order of \$10 to \$30 per square meter, but the thinner membranes might become available for about \$1 per square meter, given decreased chemical requirements and new techniques arising from vastly increased scale of production. The capital cost of the membranes would then be \$590 per kilowatt. The cost of the rest of the system, including site-specific variables such as conveyance channels and breakwaters, is hard to estimate but might approximately equal that of the membranes. In some situations facilities and structures might be shared with other elements of a water-use system. For comparison, the capital cost of commercial hydroelectric power is about \$500 per kilowatt (*14*).

Electrodialysis membranes can be used for 5 to 10 years, depending on conditions, but there are reasons to expect significantly longer life in the dialytic battery (*15*). Assuming a 10-year lifetime, the contribution of membranes to the cost of power would be approximately 0.97 cents per kilowatt-hour (*16*). As a point of reference, residential electric rates are typically 2 to 4 cents per kilowatt-hour, a figure which includes many other costs besides those of power generation.

A dialytic battery plant using only a small portion of river flow and pumping the effluent to sea would have little effect on natural habitats or on human communities nearby. On the other hand, a plant harnessing most of the available salinity power could alter the estuarine environment profoundly by eliminating tidal wash and salinity intergrading. The electrode reactions generate modest amounts of hydrogen and chlorine, and the manufacture of components would constitute a source of industrial pollution, but the membrane process itself generates no significant heat or other pollutants. Overall, the dialytic battery should be a very clean process for power generation.

In evaluating an infant technology, one should probably begin on an optimistic note to avoid discarding ideas prematurely. But we do wish to sound several warnings. First, domestic river flow is not nearly sufficient to satisfy current energy demand in the United States. The dialytic battery should be considered an adjunct to efforts in other directions, or for smaller-scale use in special situations and perhaps in less developed areas of the world. Second, power generation will not be the most effective use of fresh water where the water itself is in demand for industrial, agricultural, or personal use. Third, the cost of components of the dialytic battery will increase along with that of energy, although not necessarily in direct proportion. In conclusion, large-scale energy conversion by the dialytic battery may become practical, but only with major advances in the manufacture of ion exchange membranes and with careful optimization of operating conditions.

JOHN N. WEINSTEIN

Laboratory of Theoretical Biology,
National Cancer Institute,
National Institutes of Health,
Bethesda, Maryland 20014

FRANK B. LEITZ

Bureau of Reclamation,
Department of the Interior,
Denver, Colorado 80225

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5. R. S. Norman, *Science* **186**, 350 (1974).
6. G. Manecke, *Z. Phys. Chem.* **201**, 1 (1952); U.S. Patent 2,700,063 (1955).
7. G. Murphy [*Ind. Eng. Chem.* **50**, 1181 (1958)] considered a variation in which mixing of brackish and sea waters could be used directly, without electrodes, to desalinate water. K. H. Meyer and W. Straus [*Helv. Chim. Acta* **23**, 795 (1940)] had studied membrane arrays in another context.
8. (i) Minor ionic constituents can be assigned experimentally determined transference numbers; (ii) osmotic and electroosmotic water fluxes can be analyzed in the framework of irreversible thermodynamics; (iii) the effect of concentration polarization due to current passage can be approximated most simply by substituting for Eq. 1 the expression

$$V^{\mathrm{o}}_{\mathrm{stack}} = 2N\,\frac{\alpha RT}{\mathcal{F}}\ln\left(\frac{c_{\mathrm{s}} - \delta_{\mathrm{s}} I/2A\mathcal{D}}{c_{\mathrm{r}} + \delta_{\mathrm{r}} I/2A\mathcal{D}}\right)^{0.917}$$

where $\mathcal{D}$ is the NaCl diffusion coefficient, δ is an average unstirred layer thickness, and the other symbols are as defined later in the text; the exponent relates activity and concentration ratios in the range 0.001 to $0.6M$; and (iv) changes in concentration along each channel can be handled by integration or by choice of reasonable averages.
9. G. L. Wick and J. D. Isaacs, "Salinity power," *Scripps Inst. Oceanogr. Inst. Mar. Resour. Ref. 75-9* (1975); S. Loeb, *Science* **189**, 654 (1975); R. S. Norman, *ibid.*, p. 655. Hypersaline bodies of water could be used in conjunction with either brackish or sea water. Such special situations would permit higher mass transfer rates through the dilute compartments and would solve in part the problem of water pretreatment, but would also require much more selective membranes.
10. In terms of conventional cation transport numbers τ_+ [for example, see N. Lakshminarayanaiah, *Transport Phenomena in Membranes* (Academic Press, New York, 1969, p. 6)], we have $\alpha = \tau_+^{\mathrm{c}} - \tau_+^{\mathrm{a}}$. If all current passing through the anion exchanger were carried by Cl^- and all current through the cation exchanger by Na^+, then α would be unity; if neither membrane were selective, then α would be zero.
11. Electrode reactions could be chosen to yield useful products, but the first law of thermodynamics dictates that any energy so used would represent an inefficiency in power generation. Electrode cost must be considered in planning stack size.
12. F. Leitz, "High temperature electrodialysis—Phase I," *U.S. Dep. Inter. Off. Saline Water Res. Dev. Rep. No. 912* (1974).
13. Using models of flow in rectangular channels (F. Leitz, L. Marinčić, P. Johnson, J. Liston, "Effect of turbulence promoters on local mass transfer—Third report," *U.S. Dep. Inter. Off. Water Res. Technol. Res. Dev. Rep.*, in press), we calculate that such current densities can be attained in 0.1-mm channels at acceptable water pumping costs and reasonable fractional uses of the salinity potential.
14. *Hydroelectric Plant Construction Cost and Annual Production Expenses, Sixteenth Annual Supplement—1972* (Federal Power Commission, Washington, D.C., 1975).
15. First, current densities in the dialytic battery are an order of magnitude lower than in electrodialysis. Second, in the dialytic battery, polarization reduces concentration differences across the membrane instead of developing the alkaline, salt-rich layer responsible for scale formation. Finally, a leaky membrane, even one grossly torn, removes only the potential of a single cell pair rather than contaminating the product from the entire stack.
16. We assume straight-line amortization at 5 percent interest, 90 percent operating time, and running costs small by comparison.
17. Resistances were obtained by an a-c method in $0.1M$ NaCl; measurements of membrane resistance between solutions of pertinent unequal concentration are planned. The parameter α, determined from concentration potentials, varied only a few percent over the range of concentration pairs used.
18. We thank H. Viklund of Ionics, Inc., for his assistance in taking data and B. Bunow, J. Isaacs, and K. S. Spiegler for their advice on the manuscript. Experiments were performed at Ionics, Inc., Watertown, Mass. A preliminary version of the theoretical analysis was presented in San Francisco, September 1974, before the Salinity Power Study Group sponsored by the Scripps Institution of Oceanography and Oregon State University.

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Photoproduction of Molecular Hydrogen by a Plant-Algal Symbiotic System

Abstract. *The rapidly growing water fern* Azolla, *which contains a nitrogen-fixing blue-green algal symbiont, has been studied as a possible system for photoproduction of molecular hydrogen. When this plant is grown on a combined nitrogen supply, photochemically generated hydrogen can be diverted through the algal nitrogenase system, which serves as a source of molecular hydrogen generated from water. This symbiosis has several advantages as a possible biological energy conversion system.*

In the past few years, hydrogen has been considered as a renewable nonpolluting fuel, and this consideration has led to reports about its possible biological production by photosynthetic systems (*1, 2*). Two known systems for photohydrogen production, the anaerobically adapted green algal system of Franck and Gaffron (*3*) and the photosynthetic bacterial system of Gest and Kamen (*4*), require an exogenous electron donor and hence are not independent of a substrate other than water. Suitably constructed enzymatic systems containing chloroplasts can evolve hydrogen from water, but these are labile and, at present, have limited utility (*5*).

Table 1. Acetylene reduction and hydrogen evolution of *Azolla* plants grown on nitrogen-free and nitrate media. All values are nanomoles of gas formed per hour per gram of fresh plant tissue. Approximately 2 mg of nitrogen and 0.4 mg of total chlorophyll are contained in 1 g of tissue. When added, acetylene was 10 percent of the gas phase. The assay medium was the same as the growth medium.

Gas phase	Evolution (nmole hour^{-1} g^{-1})	
	Ethylene	Hydrogen
Nitrogen-fixing plants		
Argon	900	130
Argon, dark control	0	0
Argon (80 percent), O_2 (20 percent)	320	90
Nitrogen	460	0
Air	500	0
Nitrate-grown plants		
Argon	500	500
Argon, dark	0	0
Argon (80 percent), O_2 (20 percent)	340	300
Nitrogen	500	120
Air	340	120

Benemann and Weare's report (*6*) that the nitrogen-fixing blue-green alga *Anabena cylindrica* could evolve hydrogen from water opened up the possibility of finding similar nitrogenase-containing photochemical systems that are stable and useful for biological hydrogen production. The water fern *Azolla*, a rapidly growing plant that contains a nitrogen-fixing blue-green algal symbiont *Anabena azolla* within its leaf cavity (*7*), offers several advantages as a hydrogen-producing system.

Plants were grown in shallow layers of a nitrogen-free or nitrate-containing Hoagland solution (*8*) in 3-liter Fernbach flasks under constant illumination in air at 25°C. Approximately 30 g of fresh plant tissue was collected in 2 weeks from each flask, depending on inoculum size. Samples of individual plants or extracts were incubated in the light in 15-ml Erlenmeyer flasks fitted with screw caps containing