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Voltage Components at Gas Evolving Electrodes

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ABSTRACT

A general statement of voltage components at gas evolving electrodes, including ohmic losses, surface overpotential, gas concentration, and ionic concentration overvoltages, is presented. Discussed and illustrated are the means for estimating the value and measurability of each component. A subcomponent of the surface overpotential, termed hyperpolarization, a result of masking of the electrode by bubbles, is quantified. In hydrogen or oxygen evolution from sulfuric acid, the largest of the bubble-related components is the concentration overpotential, due to supersaturation of the electrolyte with dissolved gas. In carbon dioxide evolution from aluminum oxide dissolved in cryolite, ohmic effects are the most important. Hyperpolarization of the electrodes is estimated to be 2, 5 and 25 mV in hydrogen, oxygen, and carbon dioxide evolution, respectively.

Electrolytically evolved gas bubbles affect the electrical characteristics of electrochemical cells in several ways. In the bulk electrolyte, the bubbles reduce the effective conductivity of the electrolyte and, if nonuniformly distributed, make the macroscopic current density nonuniform, with a concomitant increase in the total polarization of the electrode. At the electrode surface, the effect on voltage is similarly both ohmic and kinetic, since the bubbles resist current and reduce the effective electrode area by blocking part of it. Bubbles at the electrode also relieve the supersaturation at gas evolving electrodes, both by absorbing the gas molecules from the supersaturated electrolyte near the electrode and by stirring the electrolyte to enhance mass transfer of dissolved gas away from the electrode.

Investigators of gas evolving electrodes have been interested in the electrical effects of bubbles attached to electrodes for at least 30 years. Early writers (1, 2) noted bubble effects on measurements of overpotential. Takata *et al.* (3) experimentally investigated the resistance of a chlorine gas bubble layer on electrodes by varying the distance between the reference electrode probe and the gas evolving electrode for various orientations of the electrode. Kubasov and Volkov (4), studying the voltage increase on downward facing anodes during chlorine evolution, found voltage losses as high as 3V. Hine *et al.* (5) distinguished between the bulk electrolyte and a region near the electrode containing a higher void fraction of gas than the bulk electrolyte. Haupin (6), using a scanning reference electrode to investigate the potential profile in an operating Hall cell, observed voltages attributable to bubble polarization. Kuhn (7) reviewed previous work on potential measurements at gas evolving electrodes and presented new data on the resistance of bubble layers at current densities less than 250 mA/cm^2. He concluded that the thickness of the bubble layer may be smaller than previously thought, less than 0.05 cm, as opposed to 0.3 cm. Janssen and Barendrecht (8) used impedance techniques to investigate the electrolytic resistance of solution layers at hydrogen and oxygen evolving electrodes as a function of electrode area, material, position, temperature, and pressure. Ngoya (9), experimenting with bubble layers on electrodes facing downward, such as those found in mercury-type chlorine cells and in the Hall cell for aluminum production, found that even small angles of inclination away from the horizontal (<3°) made a large difference in the resistance presented by such layers.

Theoretical treatments of the voltage losses caused by the bubble layer, including ohmic, kinetic, and thermodynamic effects, are few because solving the electrical and mass-transfer equations in the bubble layer is difficult. In fact, only the solution of Laplace's equation for a single spherical bubble tangent to an infinite planar electrode seems analytically possible (10), while numerical methods make solution of a more general case tractable (11). Closely packed arrays of bubbles attached to the electrode present significant resistance that Sides and Tobias (12) measured by experimenting with a large-scale analog of a hexagonal array of bubbles. At void fractions greater than 0.5, a downward turn in conductivity was represented by simple calculation called the "constriction model" that Lanzi and Savinell (13) extended to cover high void fractions in the bubble layer.

Increased ohmic losses are not the only electrical effects of bubbles on electrodes. Hine *et al.* (5) pointed out that bubbles screen a portion of the electrode surface; hence, a gas evolving electrode's potential may include an additional voltage increment because the local current density exceeds the superficial current density. They interpreted their experimental results in terms of a reduced area available for current. Haupin (14) also commented on the existence of this voltage component in Hall/Heroult cells. Dukovic (11) has calculated numerically the increased potential drop due to bubbles on electrodes; his analysis included ohmic, kinetic, and concentration effects.

Supersaturation of the electrolyte with product gas established a third component, concentration overpotential. Bon (15), measuring the concentrations of dissolved gas next to a hydrogen evolving electrode with hydrogen reference electrodes made of thin Pt foil, found supersaturations of 4-60 atm in the range of current densities 0.2-40 mA/cm^2. Shibata (16, 17) measured the supersaturation of hydrogen and oxygen electrodes with a galvanostatic transient technique and found a maximum supersaturation of hydrogen of 160 atm at 200 mA/cm^2 and a maximum supersaturation of oxygen of 70 atm at 100 mA/cm^2. Vogt (18) distinguished between the concentration in the bubble layer that is important for bubble growth and the concentration measured by Shibata (16, 17) and Bon (15) that determines the concentration overpotential. Recently, Janssen and Barendrecht (19), using a novel rotating ring cone electrode, found smaller supersaturations of 14 for oxygen evolution in alkaline medium; however, their results were complicated by loss of oxygen from solution as the supersaturated electrolyte flowed from the working cone electrode to the detecting ring. Supersaturations on the order of 100 are well established by these studies, at least for aqueous solutions.

Despite the importance of the electrical effects of gas bubbles and the volume of work devoted to the study of these effects, an overall discussion of the voltage components at a gas evolving electrode and a discussion of the measurability of the various components is lacking. While individual components of the voltage statement have been explored and quantified, a comprehensive discussion is absent. In this contribution, we write a component statement of the voltage at a gas evolving electrode, quantify the components as best as possible from present knowledge, and discuss the measurability of the various components.

Statement of Voltage Components

The potential measured between a hypothetical gas evolving electrode and a reference electrode of the same

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kind placed just outside a sheath of bubbles covering the electrode can be expressed by

$$\Delta\Phi_T = V_w - \Phi_r \quad [1]$$

where V_w is the potential of the working electrode and Φ_r is the potential of the reference electrode. Expressing the potential difference in terms of the voltage components gives

$$\Delta\Phi_T = \Delta\Phi_{ohm} + \eta_s + \eta_{cs} + \eta_{ci} \quad [2]$$

The first term on the right-hand side of Eq. [2] is the ohmic potential difference between any point on the electrode and the reference electrode, the second term is the local surface overpotential for chemical reaction and/or charge transfer reaction, and the third and fourth terms are the local concentration overpotentials that may arise from supersaturation of the electrolyte near the electrode with product gas and from depletion of the reacting ion at the electrode. These four terms vary from point to point on the surface of the electrode, but their sum must always be $\Delta\Phi_T$. Distinguishing among the four components of the experimentally measured voltage is a complicated problem, but necessary if one wishes, for example, to obtain meaningful values for the surface overpotential as a function of current density for a gas evolving electrode, or if one wishes to estimate the total voltage drop at an electrode.

The local values of the voltage components in Eq. [2] are difficult, if not impossible, to obtain, but the average values may be accessible. Equation [2] can be written as

$$\Delta\Phi_T = \overline{\Delta\Phi}_{ohm} + \bar{\eta}_s + \bar{\eta}_{cs} + \bar{\eta}_{ci} \quad [3]$$

where $\overline{\Delta\Phi}_{ohm}$ is an average ohmic voltage, loss, $\bar{\eta}_s$ represents an average over the distribution of surface overpotentials accompanying the nonuniform current distribution, and $\bar{\eta}_{cs}$, $\bar{\eta}_{ci}$ represent averages over the distribution of concentration overpotentials arising from product gas supersaturation or concentration polarization of the reacting ions. Equation [3] describes the general case in which all the possible components at an electrode are important. We discuss the components of this equation by first simplifying it to the minimum and then rebuilding it component by component. At each stage, equations for estimation of the components are discussed.

Ohmic losses due to bubbles.—If the electrode reaction is reversible, if product gas does not supersaturate the electrolyte near the electrode, and if no ionic concentration differences exist, Eq. [3] simplifies to

$$\Delta\Phi_T = \overline{\Delta\Phi}_{ohm} \quad [4]$$

The potential drop between the working and reference electrodes is entirely ohmic and exactly equals the product of the total current with the resistance based on the primary current distribution with bubbles present. This is the ohmic drop measured by current interruption in this case.

Estimation of the potential drop requires knowledge of the electrical conductivity of the bubble layer either from theory or experiment. Most of the efforts to date have aimed at quantifying this term. The ohmic voltage loss associated with the presence of the bubbles on the electrode is

$$\overline{\Delta\Phi}_{ohm} = \frac{iL(1 - K_m)}{\kappa K_m} + \frac{iL}{\kappa} \quad [5]$$

where i is the superficial current density, L is the thickness of the bubble layer, κ is the intrinsic conductivity, and K_m is the ratio of the effective conductivity to the electrolyte's intrinsic conductivity and can be estimated from the work of Sides and Tobias (12), if the void fraction in the layer and the thickness of the layer is known. The voltage loss that would occur, were the bubbles not there, is the second term on the right; Eq. [5] represents the total ohmic loss to a reference electrode placed just outside the bubble layer.

Gas bubbles and surface overpotential.—If the hypothetical electrode reaction is not reversible, but the electrolyte again is not supersaturated with the product gas, one must add a second component to the right side of Eq. [4] yielding

$$\Delta\Phi_T = \overline{\Delta\Phi}_{ohm} + \bar{\eta}_s \quad [6]$$

The voltage now consists of ohmic and electrode kinetic losses. This corresponds to a secondary current distribution around the bubbles on the electrode.

The ohmic component is again exactly given by Eq. [5], and equals the ohmic loss yielded by current interruption (20). The term $\bar{\eta}_s$ must be the sum of the surface overpotential due to the electrode reaction if no bubbles were present (*i.e.* if the electrode were operated at a microscopically uniform current density), and an amount of voltage due to an effectively higher current density that must exist because the bubbles cause a nonuniform current distribution on the electrode surface. This sum can be expressed by

$$\bar{\eta}_s = \eta_{so} + \eta_h \quad [7]$$

where η_{so} stands for the surface overpotential accompanying the uniform superficial current density if no bubbles were present, and η_h stands for the portion of the surface overpotential related to the nonuniform current density, hereafter referred to as the hyperpolarization of the electrode. One can estimate the value of η_{so} if the bubble-free Tafel constants are known, for example, from studies at low current densities. Remaining, however, is the problem of estimating a value for the hyperpolarization.

A model for understanding and quantifying hyperpolarization is based on the effective area available to the current. If the gas evolving reaction is characterized by the Tafel constants a and b on a given smooth surface in the absence of gas bubbles, then

$$\eta_{so} = a + b \log\left(\frac{I}{A}\right) \quad [8]$$

where I is the total current and A is the actual electrode area. In the spirit of Hine's work (5, 21), in which the effective electrode area was reduced by the bubbles, one may assume that, with bubbles present, there must be an effective electrode area available for current flow to the electrode, A_h, that is smaller than A, the superficial electrode area. The total surface overpotential in the presence of gas bubbles can now be expressed by

$$\bar{\eta}_s = a + b \log\left(\frac{I}{A_h}\right) \quad [9]$$

Substituting Eq. [8] and [9] into [7] and solving for η_h, one obtains

$$\eta_h = b \log\left(\frac{A}{A_h}\right) \quad [10]$$

Thus, bubbles on an electrode introduce an additional current-dependent term in the kinetic equation. A_h can be a function of the exchange current density, temperature, kinetic transfer coefficients, the average bubble diameter, and the void fraction, all of which determine the secondary current distribution on the electrode.

Values of A_h can be determined from experiments or by calculation of the secondary current distribution on the electrode. To determine A_h experimentally, one must measure the overpotential at a gas evolving electrode, with and without the bubbles being present. This is possible with special precautions, such as use of a rotating electrode to remove most of the bubbles from the surface (29). To calculate the hyperpolarization for a system with no supersaturation by product gas and with no ionic concentration gradients, one must solve Laplace's equation with kinetic boundary conditions for the secondary current distribution (11). The hyperpolarization is the difference between the calculated surface overpotential at the

position of the superficial average current density with bubbles present and the surface overpotential with no bubbles present. This difference reflects the constriction of the current to effectively smaller areas. A_h can then be calculated from Eq. [10].

A_h is always less than unity, even when the bubbles are mathematically tangent to the surface. If the bubbles are perfect spheres, tangent to the electrode at an infinitely small point, the reduction of the effective area reflects the nonuniformity of the current distribution. If the bubbles are not perfectly spherical, they mask some portion of the electrode that is also subtracted from A. A and A_h are identical only when the bubbles are perfect spheres, and the current distribution is uniform because of infinitely slow kinetics.

Some insight into the problem is afforded by dimensional analysis. Newman (22) has shown that two parameters characterize nonuniform secondary current distributions in the general case of surface kinetic limitations, but no concentration effects

$$J = \frac{(\alpha_a + \alpha_c) i_o d_d \mathbf{F}}{\kappa RT} \quad [11]$$

$$\delta = J \frac{i_{avg}}{i_o} \quad [12]$$

where: α_a = anodic transfer coefficient, α_c = cathodic transfer coefficient, i_o = exchange current density, d_d = diameter of the rotating disk, $\mathbf{F}$ = Faraday's constant, R = gas constant, and T = temperature in K. These parameters arise from the boundary conditions on Laplace's equation when finite kinetic rates are included. The first parameter, J, is a ratio between the exchange current density and ohmic parameters, such as length and conductivity. The second parameter, δ, is a dimensionless current level. Values of J or δ greater than unity indicate that the reaction kinetics are fast: therefore, the current distribution is limited by the electrolyte conductivity. Since ohmic factors are dominant, a nonuniform primary current distribution is present. When both J and δ are much less than one, the reaction kinetics are slow and a uniform secondary current distribution is present. Even though a low value of J indicates substantial kinetic effects, the current distribution resembles the primary case at high values of δ because the linear ohmic dependence on current density dominates the logarithmic overpotential dependence.

These quantities can readily be applied to bubbles on an electrode if the radius of the bubbles is used as the length parameter. For aqueous gas evolution, the values of J are less than unity due to small exchange current densities (10^{-5}), but the value of δ may be near unity, an indication that the actual microscopic current distribution may be more uniform than the primary current distribution at low current densities, and nonuniform at substantial current densities. Hyperpolarization of the electrode may be present when the value of δ is greater than unity (the current distribution is nonuniform), even if the bubbles are perfect spheres tangent to the electrode. Of course, if the contact angle of the bubbles with the electrode is greater than zero, there will be hyperpolarization simply because the bubble directly masks a portion of the electrode equal to the cross-sectional area of the bubble. We stress again that these arguments are strictly valid only when supersaturation of the electrolyte by-product gas is not important and there are no ionic concentration gradients in the bubble layer.

Concentration overpotential.—If the reaction is not reversible and the product gas supersaturates the electrolyte at the electrode surface, but there are still no ionic concentration gradients, the potential of a gas evolving electrode is given by Eq. [13], which includes ohmic and electrode kinetic losses, and concentration overpotential due to supersaturation of the electrolyte with dissolved gas

$$\Delta\Phi_T = \overline{\Delta\Phi}_{ohm} + \bar{\eta}_s + \bar{\eta}_{cs} \quad [13]$$

This corresponds to a complicated tertiary current distribution around the bubbles on the electrode.

One may still calculate the ohmic drop using Eq. [5] because ionic concentration gradients are still assumed negligible. The ohmic drop so calculated again corresponds to the voltage measured by current interruption. The average surface overpotential comprises again the η_{so} and η_h. The effective supersaturations determined by experiments such as those by Bon (13), Breiter (2), and Shibata (14, 15) allow estimation of an average concentration overpotential, if the supersaturations have been determined for the desired reaction. For example, the following equation gives the overpotential due to supersaturation of an aqueous solution by-product hydrogen gas

$$\bar{\eta}_{cs} = \frac{-RT}{2\mathbf{F}} \ln p^* \quad [14]$$

where p^* is the supersaturation ratio and n is the number of equivalents per mole.

In this case, as in the case of no concentration potential, the hyperpolarization, and hence A_h, can be calculated directly, if the tertiary current distribution, with no ionic concentration gradients, is available. The procedure would be the same as that outlined in the discussion of the secondary distribution. For electrolytic gas evolution, this is nearly impossible given the nature of the process; hence, experiments to determine η_h are necessary.

General case.—In the general case, all of the terms of Eq. [3] exist; not only are there surface overpotentials and gas-related concentration overpotentials, but depletion of the reactant in the electrolyte near the electrode causes ionic concentration overpotential, and leads to a more complicated expression for the ohmic loss term if the electrolyte is not supported. In this case, a well-defined separation of the ohmic loss from the overpotentials is not possible; however, an estimate of the voltage components can be made from the relations already cited and from experimental data available for some systems presented by investigators of mass transfer (23-27). Knowing the effective boundary layer thickness at a given rate of gas evolution and the bulk concentration of the reactant, one can calculate the surface concentration of reactant and use this to estimate the ionic concentration overpotential for the reaction. For example, when there is an effective diffusion layer of thickness δ_m, the limiting current density for hydrogen evolution and concentration overpotential, due to a concentration difference of protons in sulfuric acid, can be estimated from (assuming only protons and bisulfate ions are present)

$$i_{lim} = \frac{-\mathbf{F}DC^B}{(1 - t_+)\delta_m} \quad [15]$$

and (22)

$$\bar{\eta}_{ci} = \frac{2RT}{\mathbf{F}} \left[\ln\left(1 - \frac{i}{i_{lim}}\right) + t_+ \left(\frac{i}{i_{lim}}\right) \right] \quad [16]$$

where $\mathbf{F}$ = Faraday's constant, D = diffusivity of sulfuric acid, C^B = bulk concentration of sulfuric acid, δ_m = mass-transfer boundary layer thickness, R = gas constant, T = temperature, t_+ = transference number of the protons, i = current density, A/cm^2, and i_{lim} = limiting current density, A/cm^2.

Application to Gas Evolving Reactions

Estimates of voltage components in aqueous and molten salt electrolysis.—We now estimate the voltage components of the bubble layer for hydrogen and oxygen evolution in 1N sulfuric acid and carbon dioxide evolution in Hall-Heroult electrolysis. For this calculation, only the voltages added by the presence of the bubbles are included. The bubble-free ohmic loss within the bubble layer and the bubble-free surface overpotential are excluded. The values chosen for the parameters of the

equations are taken from cited sources, unless the value has not been measured. Equation [17] represents the ohmic voltage loss associated with the presence of the bubbles on the electrode. Note that the voltage loss that would occur, were the bubbles not there, has been subtracted

$$\overline{\Delta\Phi}_{ohm} = \frac{iL(1 - K_m)}{\kappa K_m} \quad [17]$$

Hyperpolarization of the electrode is calculated from Eq. [10] with estimated values for the effective area available for current.

The gas-related concentration overpotential is calculated from Eq. [14] for hydrogen evolution, where activity coefficients have been ignored for the purposes of this rough estimate. The corresponding equation for oxygen evolution and for carbon dioxide evolution is

$$\bar{\eta}_{cs} = \frac{RT}{4\mathbf{F}} \ln p^* \quad [18]$$

The ionic concentration overpotentials for hydrogen evolution are calculated from Eq. [15] and [16]]. For oxygen evolution, the appropriate equations are

$$i = \frac{-\mathbf{F}D(C^B - C^s)}{(1 - t_+)\delta_m} \quad [19]$$

and (22)

$$\eta_{ci} = \frac{2RT}{\mathbf{F}} \left[\ln \frac{C^s}{C^B} + t_+ \left(1 - \frac{C^s}{C^B} \right) \right] \quad [20]$$

where C^s = surface concentration of sulfuric acid. In the Hall cell for aluminum production, the corresponding equations are

$$i_{lim} = \frac{4\mathbf{F}DC^B}{\delta_m} \quad [21]$$

and

$$\bar{\eta}_{ci} = \frac{RT}{2\mathbf{F}} \ln \left(1 - \frac{i}{i_{lim}} \right) \quad [22]$$

The results of these calculations appear in Table I. In aqueous hydrogen and oxygen evolution, the components sum to 70 and 40 mV, respectively, and the largest contribution is from supersaturation of the electrolyte with product gas. Masking of the electrode by bubbles causes an overpotential proportional to the logarithm of the surface coverage, which is a weak dependence. Hyperpolarization may be responsible for small but measurable amounts of polarization at gas evolving electrodes. In the molten salt cell, the high current density and thick bubble layer underneath the carbon anodes cause a substantial ohmic loss that dominates the other components.

Measurability of the voltage components.—Most industrial gas evolving reactions fall into the category of having ohmic, hyperpolarization, and gas concentration effects as contained in Eq. [13]. Ionic concentration overpotential is probably negligible in the concentrated solutions that are industrially practical. Measurable in the circumstances of no ionic gradients is the combined total of the surface overpotential and the gas concentration overpotentials, because current interruption gives the ohmic portion equivalent to the resistance, based on the primary current distribution multiplied by the total current. Subtracting the ohmic component from the total measured voltage yields the sum of the average surface overpotential, and gas-related concentration overpotential. Separating the concentration overpotential and hyperpolarization from the bubble-free kinetic component, however, requires additional measurement of the potential, with and without the bubbles present. Without special techniques to eliminate the effects of current distribution and overcome the problem of supersaturation near the electrode, the hyperpolarization may not be explicitly subtracted. In particular, kinetic measurements at low current densities may be subject to error if precautions are not taken to remove slowly growing bubbles and minimize and/or detect and measure the supersaturation of the electrolyte by dissolved gas.

Table I. Gas evolution parameters and voltage components of the bubble layer

Parameter[a]	H_2 1*M* H_2SO_4[a,b]	O_2 1*M* H_2SO_4[a,b]	CO_2 Na_3AlF_6,Al_2O_3[a,b]
i	−0.1	0.1	1
L	0.05 (?)	0.05 (?)	0.5 (28)
κ	0.3	0.3	2.5
f	0.25 (?)	0.25 (?)	0.5 (?)
K_m (12)	0.67	0.67	0.4
n	2	4	4
p^*	100 (15)	80 (17)	100 (?)
T	298	298	1273
A/A_h	1.03 (29)	1.1(?)	1.25 (29)
b	−0.12	0.12	0.26 (29)
δ	100 (25)	50 (25)	50 (?)
C^B	0.001	0.001	0.00068
t_i	0.88	0.88	0
D (10^5)	2.33	2.33	5. (?)
Component (V)			
$\overline{\Delta\Phi}_{ohm} - iL/\kappa$	−0.009	0.009	0.300
$\bar{\eta}_h$	−0.002	0.005	0.025
$\bar{\eta}_{cs}$	−0.059	0.028	0.028
$\bar{\eta}_{ci}$	−0.0004	0.0002	0.026
Total	−0.070	0.042	0.379

[a] Numbers in parentheses indicate references for the quantities.
[b] (?) indicates estimate by writers in the absence of data.

Conclusions

The voltage statement for a gas evolving electrode consists of ohmic, kinetic, and thermodynamic components. While it is simple to write a voltage component statement for a gas evolving electrode, isolating and quantifying the average values of the components is complex, but there is now enough information in the literature to make approximate prediction of the voltage components possible, according to the equations presented.

Under most circumstances in aqueous gas evolution, it appears that supersaturation of the electrolyte is the principal voltage component, other than the pure charge transfer overpotential. Ohmic losses and kinetic losses due to masking of the electrode appear to be small by comparison. In molten salt electrolysis, such as practiced in the Hall cell for aluminum production, the ohmic component is probably the largest direct effect of the gas bubbles, with the other components contributing an order of magnitude smaller amount.

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LIST OF SYMBOLS

a	Tafel intercept, V
A	superficial area of a gas evolving electrode, cm^2
A_h	area available for current flow on a gas evolving electrode, cm^2
b	Tafel slope, V
C^B	bulk concentration of diffusing ionic species, mol/cm^3
D	ionic diffusivity, cm^2/s
L	thickness of a bubble layer, cm
f	void fraction
$\mathbf{F}$	Faraday's constant, C/equiv.
i	current density, A/cm^2
i_{avg}	superficial current density, A/cm^2
i_0	exchange current density, A/cm^2
I	electric current, A

J polarization parameter
K_m ratio of the effective conductivity to the conductivity of the continuous medium
n number of equivalents per mole
p^* supersaturation ratio of dissolved gas
V_w voltage of the working electrode, V
α_a anodic transfer coefficient
α_c cathodic transfer coefficient
δ dimensionless current level, polarization parameter
δ_m mass-transfer boundary layer thickness, μm
$\Delta\Phi_{ohm}$ local ohmic voltage drop between the electrode and the reference electrode, V
$\overline{\Delta\Phi}_{ohm}$ average ohmic voltage drop between the electrode and the reference electrode, V
$\Delta\Phi_T$ voltage measured between the working electrode and a reference electrode of the same kind, V
η_{ci} ionic concentration overpotential at the working electrode, V
$\overline{\eta}_{ci}$ average ionic concentration overpotential, V
η_{cs} gas concentration overpotential at the working electrode, V
$\overline{\eta}_{cs}$ average gas concentration overpotential at the working electrode, V
η_h hyperpolarization of the working electrode due to nonuniform current distribution associated with the presence of gas bubbles, V
η_s surface overpotential at the working electrode, V
$\overline{\eta}_s$ average surface overpotential at the working electrode, V
η_{so} surface overpotential of the working electrode if no bubbles were present and the electrode operated at the superficial current density, V
κ intrinsic electrolyte conductivity, mho/cm
Φ_f potential of a reference electrode of the same kind as the working electrode

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Halide and Sulfate Ion Diffusion in Nafion Membranes

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ABSTRACT

The self-diffusion coefficients of chloride, iodide, and sulfate anions have been measured in Nafion® perfluorosulfonate and perfluorocarboxylate membranes using radiotracer methods. Values were measured with the membranes in equilibrium with hot, concentrated brine and caustic solutions which are typical of brine electrolysis cells, and also in dilute solution environments. Several differences were found for these diffusion coefficients, and those of cations measured previously, compared to conventional ion exchange polymers. It is postulated that separate diffusional pathways exist for cations and anions in these polymers, and that this feature contributes to the high permselectivity which these polymers exhibit.

A rather substantial literature has developed over the past few years on the properties of perfluorinated ionomer membranes, such as the Nafion® brand of polymers. Their importance in the chlor-alkali industry is now well established as a result of steady improvements in membrane cell power consumption, due both to innovations in polymer synthesis and membrane fabrication and in cell design. In this and other applications such as solid polymer electrolyte fuel cells, the high ionic conductivity, remarkable permselectivity, and excellent chemical stability of these membranes compensate for their rather high cost. In other potential membrane applications, this cost presents a barrier however, and so it would be desirable to develop analogous, less expensive materials with similar transport properties even if some of this chemical stability were lost.

In order to achieve this goal, it is important to develop as detailed an understanding as possible about the underlying relationship between polymer structure and transport properties. This knowledge would help to guide the synthesis of new membrane materials for electrolytic and other separation applications. A second motivation for this research involves the inherent scientific importance of the perfluorinated ionomers. Ionomers are ion-containing polymers which show a spontaneous organization of ionic sites and counterions into dipole multiplets and for some materials into larger ion clusters containing fifty or more pairs of ions. The perfluorinated ionomers are of the latter type, and their unusual and useful transport properties are a direct result of this equally unusual morphology. In general, ionomers pos-

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