

Current-voltage curves of bipolar membranes

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Bipolar membranes consist of a layered ion-exchange structure composed of a cation selective membrane joined to an anion selective membrane. They are analogous to semiconductor p - n devices as both of them present current-voltage curves exhibiting similar rectification properties. In this article, we present some current-voltage curves obtained for different bipolar membranes at several temperatures. The results can be interpreted in terms of a simple model for ion transport and field-enhanced water dissociation previously developed. The mechanism responsible for water splitting is assumed to be a catalytic proton transfer reaction between the charged groups and the water at the membrane interface. The effects of temperature are taken into account by introducing an Arrhenius-type relationship for the dependence of the forward rate constant of the reaction on temperature. Finally, comparison between theory and experiments provides reasonable values for the parameters introduced in the theoretical model. The analysis aims at developing a better physical understanding of a process in which chemical reactions and transport phenomena are coupled in such a way that the potential technological applications depend strongly on this coupling.

INTRODUCTION

Bipolar membranes are composed of one cation and one anion selective layers joined together in series. The electrical behavior of these systems resembles that shown by the semiconductor p - n junctions, as both of them exhibit similar rectification properties.¹⁻⁴ There exist, however, some differences between semiconductors and bipolar membranes,³ the main being the nature and number of the charge carriers. While in solid state devices there exist only two carriers (electrons and holes), in bipolar membranes at least four ionic species should be considered: the two ions arising from a surrounding salt solution fully dissociated and the OH^- and H^+ ions generated under reverse bias conditions by the high electric field existing at the interface between the two selective layers. The actual origin of the OH^- and H^+ field-enhanced generation, referred to as water splitting, is a matter of controversy: there have been several hypotheses proposed—the second Wien effect,⁴ the existence of a neutral layer at the interface of the membrane⁵—but it seems to be proved⁶⁻⁸ that the generating mechanism is a field-enhanced chemical reaction of protonation and deprotonation involving ionizable groups and water at the membrane interface. Space-charge and ion transport effects strongly influence this mechanism.

Synthetic bipolar membranes are receiving much attention nowadays because of their increasing importance for several industrial purposes. In fact, the ability of bipolar membrane technology to convert selective industrial wastes (acids, alkalies, or salts) into valuable products that can be recycled and reused seems to be proved.⁹⁻¹¹ In this sense, the temperature effects on the degree of water splitting in the bipolar membrane can play an important role in

the design and improvement of the equipment used. It has also been observed that monolayer ion exchange membranes employed in electro dialysis stacks can show a behavior similar to that of bipolar membranes because of the deposition of charged impurities on its surface.^{12,13} On the other hand, many physiological membranes containing fixed charges can be approximately analyzed by means of simplified bipolar membrane models.^{1,2}

In this article we present current-voltage curves obtained for different bipolar membranes at several temperatures. The results can be interpreted in terms of a simple model for ion transport and water splitting previously developed.^{14,15} The mechanism responsible for water splitting is assumed to be a catalytic proton transfer reaction between the charged groups and the water at the membrane interface, and the effects of temperature are taken into account by introducing an Arrhenius-type relationship for the dependence of the forward rate constant of the reaction on temperature.¹⁵⁻¹⁷ Finally, comparison between theory and experiments provides reasonable values for the parameters appearing in the theoretical model employed.

The study of ion transport and water splitting in bipolar membranes involves a number of concepts from physics and chemistry, and has a direct impact on engineering problems. This analysis aims at developing a better understanding of a process in which chemical reactions and transport phenomena are coupled in such a way that the potential technological applications depend strongly on this coupling. In this sense, our article can be of interest in a field where economic and technological pressures may sometimes favor “trial and error” procedures rather than basic studies of the physical phenomena involved.

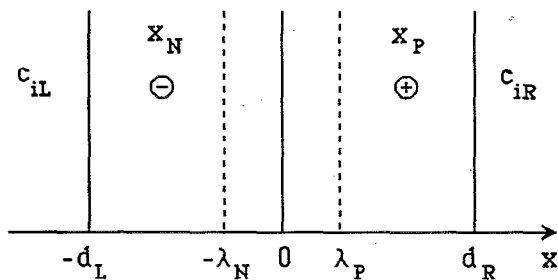


FIG. 1. Sketch of the bipolar membrane. The region extending from $x = -\lambda_N$ to $x = \lambda_P$ corresponds to the space-charge layer between the negatively and positively charged layers.

THEORY

Let us consider the bipolar membrane shown in Fig. 1. The membrane consists of two ion-selective regions, each one containing a homogeneous distribution of fixed charges. The cation-exchange layer has a negative fixed charge concentration X_N and lies from $x = -d_L$ to $x = 0$, while the anion-exchange layer extends from $x = 0$ to $x = d_R$ and contains a positive fixed charge concentration X_P . The membrane separates two salt solutions, being c_{ik} the molar concentrations of the mobile ions in the different regions of the system ($i = 1, 2, 3, 4$ denote, respectively, the salt cation, the salt anion, the hydrogen ion, and the hydroxyl ion, while $k = L, R, N, P$ stand for the left and right bulk solutions and the cation and anion selective layers, respectively).

In the isothermal quasiequilibrium steady state, inner and outer ion concentrations at the membrane/solution interface are related by the Donnan equilibrium conditions.¹⁸ On the other hand, in the bulk of the two ion exchange layers, the ion concentrations must obey the electroneutrality equation (note that membrane thicknesses d_L and d_R are assumed to be much greater than the typical Debye length¹⁹ of the problem). When the bipolar membrane is under reverse bias conditions, a thin region at the membrane interface located at $x = 0$ becomes almost completely devoid of mobile ions,³ and electroneutrality fails within. This space-charge zone, extending from $x = -\lambda_N$ to $x = \lambda_P$ in Fig. 1, shows an electrical behavior close to that exhibited by the p - n abrupt junctions appearing in some solid-state semiconductor devices,^{1-3, 20} and any externally applied voltage will appear as a potential drop across it. By applying the results obtained by Shockley^{20,21} for a p - n junction to our case, the electric field at the junction, E , and the thickness of the space charge zone, λ , are

$$E = \left(\frac{2RT}{\epsilon_r \epsilon_0} (\Delta\tilde{\Psi}_M - \tilde{V}) \frac{X_N X_P}{X_N + X_P} \right)^{1/2}, \quad (1)$$

$$\lambda = \lambda_N + \lambda_P = \left(\frac{2\epsilon_r \epsilon_0 RT}{F^2} (\Delta\tilde{\Psi}_M - \tilde{V}) \frac{X_N + X_P}{X_N X_P} \right)^{1/2} \quad (2)$$

where ϵ_0 is the permittivity of the free space, $\epsilon_r = \epsilon/\epsilon_0$ the dielectric constant of the membrane, and $\tilde{V} \equiv (F/RT)V$ is the dimensionless externally applied potential (F is the Faraday constant, R the gas constant, and T the absolute

temperature). $\Delta\tilde{\Psi}_M$ denotes the dimensionless membrane potential arising from the concentration difference between the two bulk solutions.^{2,22} Since usual membranes have $X_N \approx X_P \approx 1$ M and $\epsilon_r \approx 20$,⁷ typical values for E and λ would be some 7×10^8 V/m and 2×10^{-9} m, respectively, for a potential difference of 1 V applied under reverse bias. A chemical reaction of protonation and deprotonation between ionizable groups and water can be accelerated by the presence of such a high electric field at the membrane surface, as suggested previously by Simons.⁶ In fact, if we consider the following relationship for the forward rate constant, k_d , and the electric field:⁸

$$k_d = k_d^0 \exp\left(\frac{\alpha F}{RT} E\right), \quad (3)$$

where k_d^0 is the forward rate constant at equilibrium conditions and α is a characteristic parameter having the dimensions of length (typically⁸ $\alpha \approx 10^{-10}$ m), then the ratio k_d/k_d^0 is of the order of 20. According to Simons,⁷ this enhancement of the forward rate constant would be enough to explain the water splitting phenomenon. On the other hand, under forward bias conditions, the electric field will not be strong enough to increase k_d significantly and the electric current will be carried by the salt ions and the OH^- and H^+ ions generated under equilibrium conditions. Experiments show that this is indeed the case.²³

In order to determine the fluxes of the mobile charge carriers, the Nernst-Planck equations together with the continuity equations must be solved in each part of the system under the appropriate boundary conditions. A complete description of the solution procedure and main simplifying assumptions can be found in Refs. 14 and 15. However, the experimental results presented here were obtained using a Na_2SO_4 solution, while the theoretical model there included was developed for a uni-univalent electrolyte (NaCl , for example). Similar calculations show that the current-voltage curve for a membrane bathed by a 2:-1 binary electrolyte can be written in the form:

$$i = F \left(\frac{D_{1P} \bar{c}_{1P}(d_R)}{d_R} + D_{3H} \beta \bar{c}_{3P}(d_R) \coth(\beta d_R) + D_{4N} \beta_N \bar{c}_{4N}(-d_L) \coth(\beta_N d_L) \right) \left[\exp\left(\frac{FV}{RT}\right) - 1 \right] + 2F \frac{D_{2N} \bar{c}_{2N}(-d_L)}{d_L} \left[\exp\left(\frac{2FV}{RT}\right) - 1 \right] - F k_d n \lambda, \quad (4)$$

where

$$\bar{c}_{1P}(d_R) \approx c_{1R} \left(\frac{2c_{2R}}{X_P} \right)^{1/2}, \quad (5)$$

$$\bar{c}_{3P}(d_R) \approx c_{3R} \left(\frac{2c_{2R}}{X_P} \right)^{1/2}, \quad (6)$$

$$\bar{c}_{2N}(-d_L) \approx \frac{c_{2L} c_{1L}^2}{X_N^2} \left(1 + \frac{c_{3L}}{c_{1L}} \right)^2, \quad (7)$$

$$\bar{c}_{4N}(-d_L) \approx \frac{c_{4L}c_{1L}}{X_N} \left(1 + \frac{c_{3L}}{c_{1L}} \right), \quad (8)$$

$$\beta_P = [k_r^0 \bar{c}_{4P}(d_R)/D_{3P}]^{1/2}, \quad (9)$$

$$\beta_N = [k_r^0 \bar{c}_{3N}(-d_L)/D_{4N}]^{1/2}, \quad (10)$$

$$\bar{c}_{4P}(d_R) \approx c_{4R} \left(\frac{X_P}{2c_{2R}} \right)^{1/2}, \quad (11)$$

$$\bar{c}_{3N}(-d_L) \approx \frac{X_N}{1 + (c_{1L}/c_{3L})}. \quad (12)$$

In Eqs. (4)–(12) overbars denote inner membrane concentrations, D_{ik} stands for the diffusion coefficient of species i in the k region, k_r^0 for the recombination rate constant of water when no electric field is applied, and n is the concentration of active sites in the depleted layer where the reaction is taking place.⁸

The first two terms of Eq. (4) give a typical rectification curve (note that V take negative values under reverse bias conditions), and account for the current carried by the salt ions and the water ions generated under equilibrium conditions. The third term gives that part of the current due to field-enhanced water dissociation. Since the high electric field enhances water dissociation at the interface $x=0$, this term is expected to prevail as the reverse applied voltage increases, and to vanish under forward bias conditions.

Finally, the effects of temperature on water splitting can be interpreted, as a first approximation, by means of the Arrhenius equation:^{16,17}

$$k_d^0 = A \exp(-E_a/RT) \quad (13)$$

where A is called the pre-exponential factor and E_a is the activation energy of the reaction. Throughout this paper, the parameters A and E_a will be assumed to be constant. In a more general treatment, both of them may depend on temperature.^{16,17}

EXPERIMENT

The measurements of the current-voltage curves were taken in a laboratory-scale test cell designed for the production of acids and bases from their corresponding salts, which is one of the main applications of bipolar membranes.^{9,10} Figure 2(a) shows the system used. The electro dialysis cell (K), which appears in Fig. 2(b), occupies the central part of the device, and consists of six half-cells arranged in series. The side cells are separated by single anion (A) and cation (C) exchange membranes. The bipolar membrane (BM) divides the two central half-cells. When the entire electro dialysis cell is reverse biased using the working electrodes (WE), the large electric field appearing at the membrane interface produces an excess of OH^- and H^+ ions due to the field-enhanced chemical reaction. These water ions permeate the corresponding exchange layers of the bipolar membrane and enter in the adjacent 0.25 M Na_2SO_4 solutions. The consequence is the formation of an acid (H_2SO_4) in the left half-cell and a base (NaOH) in the right one. The pumps (P) maintain a

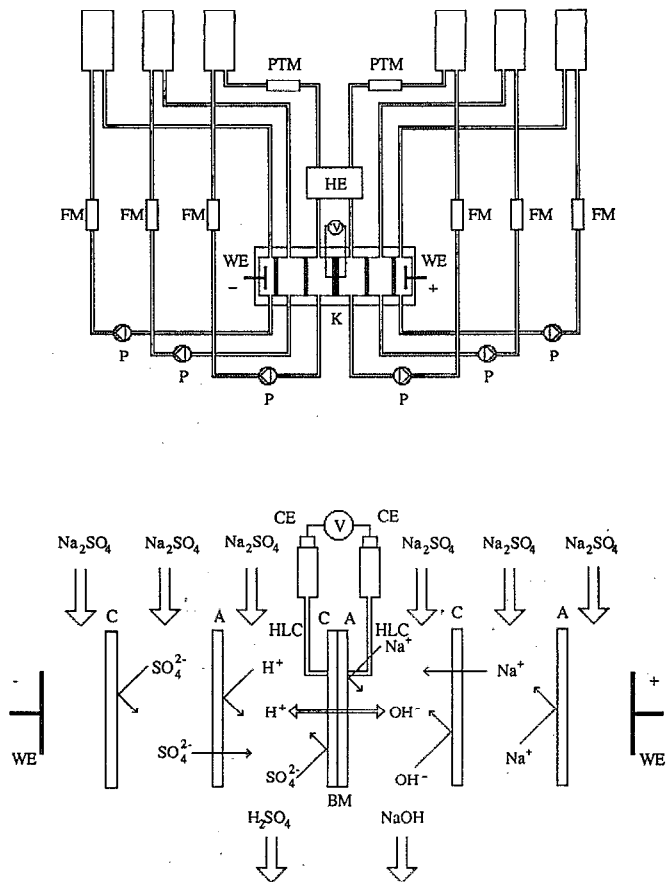


FIG. 2. Schematic representation of the experimental setup.

continuous cyclic flow of the Na_2SO_4 solutions to the electro dialysis cell, being the final result a progressive enrichment in acid and base of the entering salt solutions. The single ion exchange membranes placed close to the working electrodes are used to avoid pH changes in the electrode cells.

The electric current was supplied to the cell via a dc Gossen-Konstanter source. Nickel (cathode) and platinum (anode) electrodes were used. The potential drop across the bipolar membrane was measured using two calomel electrodes (CE) connected to a digital voltmeter (V). The calomel electrodes were in contact with the bipolar membrane surfaces through a couple of Haber-Luggin capillaries (HLC) filled with 1 N KCl solutions.²⁴ The temperature of the entering solutions was controlled using a Jucabo HCF10 thermomixer connected to coiled glass heat exchangers (HE). The pH and temperature values of the solutions were tested by means of a Tüv LF537 microprocessor pH meter (PTM). The single ion exchange membranes were commercial Stantech AMX (anion exchanger) and CMX (cation exchanger).

After a preliminary study of a number of bipolar membranes, we observed three different behaviors for the current-voltage curves under reverse bias conditions. We present here examples of these three behaviors in order to show the validity of the theoretical model employed for the different membranes examined. The membranes referred to

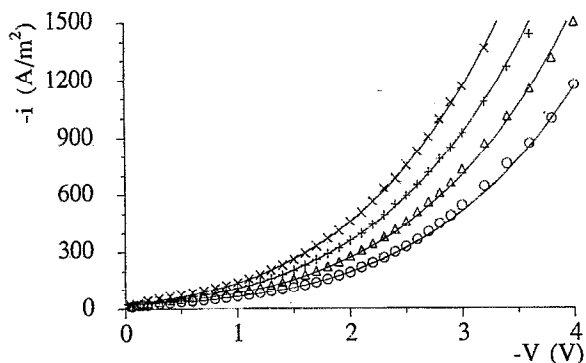


FIG. 3. Current-voltage curves for the membrane M14. The experimental points correspond to temperatures $T=292$ K (\circ), 303 K (Δ), 313 K ($+$), and 322 K (\times). The current increases with the temperature over the entire voltage range. Solid lines correspond to the theoretical results.

as M14 and M25 were prepared at the University of Stuttgart by simply laminating conventional cation and anion exchange sheets back to back.⁹ Both bipolar membranes had the same type of cation selective layer, which basically consisted of a polymer matrix with sulfonic acid fixed groups. However, both the polymer matrix and the fixed charged groups of the anion selective layers were different in membranes M14 and M25. The anion exchange layer in the membrane M14 were prepared by quaternization of a previously chloromethylated polystyrene with the tertiary amine DABCO. In membrane M25, the anion ex-

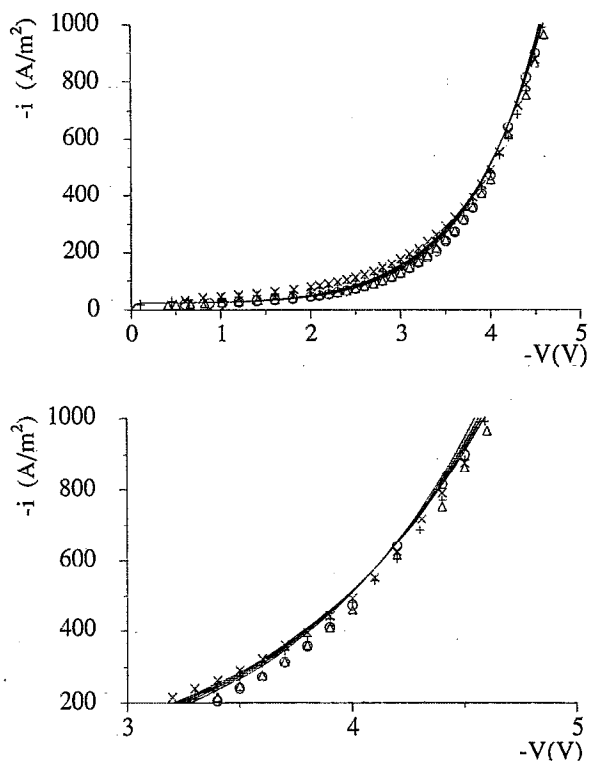


FIG. 4. Current-voltage curves for the membrane M25. The experimental points have been recorded at temperatures $T=283$ K (\circ), 294 K (Δ), 303 K ($+$), and 312 K (\times). The current increases with temperature at low voltages but decreases with temperature at higher voltages. The theoretical results (solid lines) also follow this trend.

change layer was made of polyvinylimidazole methylated. The fixed charge concentration in the two bipolar membranes were about $X_N \approx X_P \approx 1.5$ M. The thicknesses of the membranes were $d_L \approx d_R \approx 110$ μm (M14) and $d_L \approx 100$ μm , $d_R \approx 150$ μm (M25). Further details on membrane casting and physicochemical properties can be found elsewhere.^{25,26} The membrane called WSI was a commercial bipolar membrane developed at the WSI Technologies Inc. laboratories (USA). It consisted of an anion exchange region containing strongly basic quaternary ammonium groups in series to a cation exchange region having sulfonic acid groups. The thickness of the whole membrane was about $d_L + d_R \approx 115$ μm . A more detailed description of the preparation process and membrane characteristics can be found in Ref. 27.

The current-voltage curves were obtained by applying a potential difference to the system and allowing the current to reach a steady state value, which typically took a few seconds. Preceding each run, the bipolar membrane used was equilibrated for several hours with the solution employed in the experiment. As water splitting effects take place when a high electric field appears at the membrane interface, only the current-voltage curves under reverse bias conditions were considered. Under forward bias conditions water splitting becomes negligible,^{8,14} all the electric current is carried by the salt ions, and the transport phenomena lacks technical interest.

RESULTS

Figure 3 shows the experimental results obtained for the membrane M14 at different temperatures. The current-voltage curves show the typical behavior associated to a field-enhanced water dissociation caused by a chemical reaction.¹⁵ It can be also seen that the water splitting effects significantly increase with temperature. The theoretical curves (solid lines) reasonably fit the experimental data if the different parameters in Eq. (4) take the values: $nA = 1.13 \times 10^{10}$ mole $\text{m}^{-3} \text{s}^{-1}$, $\alpha = 7.3 \times 10^{-11}$ m, $E_a = 33$ kJ mole⁻¹, $\epsilon_r = 20$, $D_{ik} = 7 \times 10^{-11}$ m^2/s ($i=1,2$, $k=N, P$), $D_{ik} = 10^{-9}$ m^2/s ($i=3,4$, $k=N, P$).

The experimental current-voltage curves for the membrane M25 are shown in Figs. 4(a)–4(b). The shape and working range of each individual curve resemble those seen for the membrane M14 in Fig. 3. However, the dependence of the water splitting on the temperature is very different [see Fig 4(b)]. Indeed, we see that for membrane M25 the current increases with the temperature at low voltages, while it decreases with temperature at higher voltages. The theoretical curves (solid lines) can also account for this surprising behavior of the water splitting with the temperature if the parameters of Eq. (4) are chosen to be: $nA = 1.3 \times 10^6$ mole $\text{m}^{-3} \text{s}^{-1}$, $\alpha = 1.3 \times 10^{-10}$ m, $E_a = 23$ kJ mole⁻¹, $\epsilon_r = 20$, $D_{ik} = 10^{-10}$ m^2/s ($i=1,2$, $k=N, P$), $D_{ik} = 10^{-9}$ m^2/s ($i=3,4$, $k=N, P$).

Figure 5 shows the current-voltage curves obtained for the WSI membrane at different temperatures. The experimental results show that water splitting increases with temperature, as seen in membrane M14. On the other hand, the shape and working range of each individual

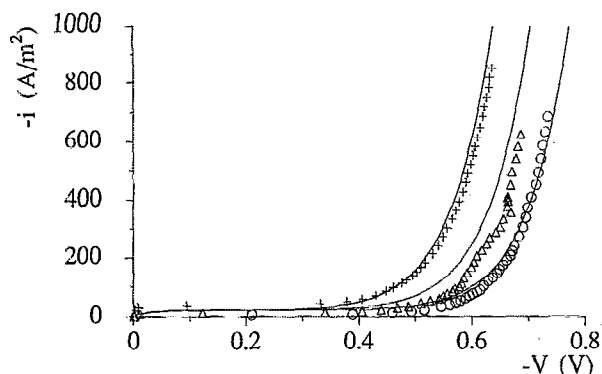


FIG. 5. Current-voltage curves for the membrane WSI. The curves have been measured at the temperatures: $T=281$ K (\circ), 299 K (Δ), and 318 K ($+$). The current increases with temperature over the entire voltage range. Solid lines correspond to the theoretical results.

curve are very different to those exhibited by the membranes M14 and M25: the WSI membrane rectifies the electric current at low voltages; suddenly, at some critical voltage, the water ions generated by water splitting begin to carry most of the current. The shape and temperature dependence of the experimental data resemble the theoretical predictions obtained by assuming a second Wien effect for the origin of water splitting.¹⁵ However, the theory based in a chemical reaction model (solid lines) can also fit the experimental data if the parameters of Eq. (4) take the values: $nA=2 \times 10^{13}$ mole $m^{-3} s^{-1}$, $\alpha=6.2 \times 10^{-10}$ m, $E_a=83$ kJ mole⁻¹, $\epsilon_r=20$, $D_{ik}=4 \times 10^{-11}$ m²/s ($i=1, 2, k=N, P$), $D_{ik}=10^{-9}$ m²/s ($i=3, 4, k=N, P$).

Finally, a local effective value of the membrane M14 resistance, \bar{R} , defined as the quotient V/i , is presented in Fig. 6. The experimental data are those shown in Fig. 3. We can see that the resistance increases first with the applied voltage, reaches a maximum value, and decreases finally towards very low values at higher voltages. This can be interpreted considering that when a low voltage is applied the rectification properties domain. The maximum value of the resistance gives the voltage from which the water splitting effects become dominant. This voltage can

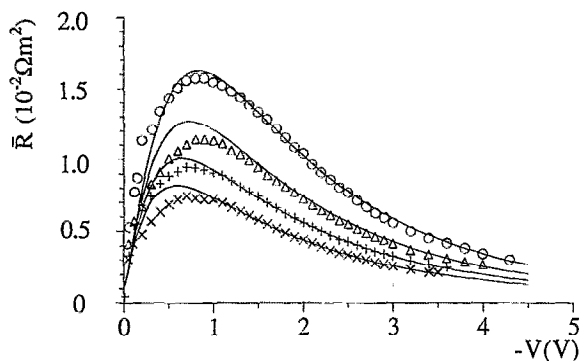


FIG. 6. The local effective value of the membrane M14 resistance (V/i) vs the applied voltage. The temperatures are $T=292$ K (\circ), 303 K (Δ), 313 K ($+$), and 322 K (\times). Solid lines represent the theoretical results.

be theoretically determined by solving numerically the equation resulting from the condition:

$$d\bar{R}/dV=0, \quad (14)$$

where i is that given in Eq. (4).

DISCUSSION

In this article we have presented three current-voltage curves showing the typical behaviors of the bipolar membranes studied. Although the shapes and temperature dependencies of the curves are different, all the experimental results can be interpreted on the basis of the same model for ion transport and water splitting. Although simple, the model can account for the nontrivial problem of the transport of four ionic species, two of them capable to generate and recombine via a field-enhanced chemical reaction. Comparison between theory and experiment provides reasonable values for the parameters (the characteristic length α , the activation energy of the chemical reaction E_a , and the product nA) involved in the theoretical model.²⁸ The other ones (the diffusion coefficients D_{ik} , the thicknesses d_k , the dielectric constant ϵ_r , and the fixed-charge concentrations X_N, X_P) can be obtained by independent measurements.^{29,30} As the first three parameters control the water splitting capacity of a bipolar membrane, a good knowledge of them should be of prime importance in order to improve the performance of the installations where bipolar membrane technology is used. Studies on the fundamentals of the chemical reactions taking place are in progress.

Finally, one interesting conclusion can be drawn from the results obtained for the membranes M14 and M25. It has been observed that single anion exchange membranes can display water splitting properties, while common single cation exchange membranes are not likely to exhibit them.^{31,32} The fact that the membranes M14 and M25 have the same cation exchange layer but *different* anion exchange layer supports the assumption that the mechanism responsible for water splitting is a chemical reaction taking place at the membrane interface on the anion exchanger side, as suggested by Simons.^{6,7} Indeed, a second Wien effect model could not explain the two different behaviors observed for the temperature dependence of the water splitting: two different chemical reactions could yield *different* temperature dependencies, but a second Wien effect would give a *similar* temperature dependence in both cases.

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