

Evaluation of a Ceramic-Polymer Composite Cation-Selective Membrane for Sodium Salt Splitting

F. Girard,^{a,c,*} R. Izquierdo,^{b,**} E. Quenneville,^{b,**} S. T. Bah,^b M. Paleologou,^{a,*} M. Meunier,^b
D. Ivanov,^{b,c,*} and A. Yelon^{b,*}

^aPulp and Paper Research Institute of Canada, Pointe-Claire, Quebec, Canada H9R 3J9

^bDépartement de Génie Physique, École Polytechnique de Montréal, Succ. Centre-Ville, Montréal, Québec, Canada H3C 3A7

A RAIPORE polymeric cation-selective membrane was modified by deposition of a thin film of NASICON, a sodium superionic conducting ceramic, using pulsed laser deposition. The composite membrane was incorporated into an electrolysis system for the production of sodium hydroxide and sulfuric acid from sodium sulfate. Its performance was compared to the unmodified polymeric base membrane. The composite membrane showed a significantly higher selectivity for sodium over hydrogen ions compared to the unmodified polymeric base membrane, resulting in a higher current efficiency and a lower energy consumption for the production of sodium hydroxide. The composite membrane was also found to be more resistant to fouling by ferric ion as compared to the polymeric membrane. Neither membrane was fouled by calcium or magnesium. The selectivity of the composite membrane for sodium over potassium ions was not found to improve by the deposition of the ceramic layer.

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Electromembrane processes such as electrolysis and bipolar membrane electrodialysis can be employed in the recovery of valuable chemicals from waste streams. These technologies have been proposed as useful unit operations for assisting kraft pulp mills achieve system closure with respect to the process elements, sodium and sulfur.¹ For instance, one of the applications proposed in the literature is the recovery of sodium hydroxide and sulfuric acid from sodium sulfate, a by-product of chlorine dioxide generators.²⁻⁵

The simplest electromembrane process, electrolysis, is illustrated in Fig. 1. A unit cell consists of two electrode compartments separated by a cation-selective membrane. One compartment, the anolyte, is usually filled with a salt-containing solution while the other compartment, the catholyte, is filled with water containing a low concentration of electrolyte to ensure the conductivity of the solution. When an electric field is applied between the two electrodes, alkali metal ions are driven toward the cathode while the anions migrate toward the anode. Electroneutrality is maintained by the decomposition of water at the electrode surfaces forming oxygen gas and protons at the anode and hydrogen gas and hydroxide anions at the cathode. Once the alkali metal ions from the anolyte cross the cation-selective membrane, represented in Fig. 1 by a circled plus sign, they combine with the hydroxide ions produced at the cathode to form the corresponding base in the catholyte. The migrating alkali metal ions in the anolyte are replaced by the protons produced at the anode thereby forming the corresponding acid of the salt that was originally placed in this compartment.

In such systems, the performance of a membrane is evaluated through the measurement of the current efficiency for the production of sodium hydroxide and the voltage drop across the membrane. Current efficiency is defined as the portion of the current that is being consumed in useful work (to make the desired products). Operationally, it is defined as the ratio of the actual over the theoretical chemical (acid or base) production rate as calculated according to Faraday's law. The current efficiency in electrolytic systems incorporating polymeric membranes is limited by their low selectivity for sodium over hydrogen ions. Another limitation related to selec-

tivity encountered with polymeric cation-selective membranes is fouling by multivalent metal ions. These tend to precipitate inside the membrane in the form of insoluble hydroxide salts, thereby leading to an increase in voltage across the membrane and ultimately shortening its operational life.⁶

Recently, a different type of cation-selective membrane based on ceramic materials was reported for sodium salt splitting.⁷⁻¹⁰ These ceramic membranes are based on NASICON sodium-ion conducting ceramics previously developed to be used as solid electrolytes in

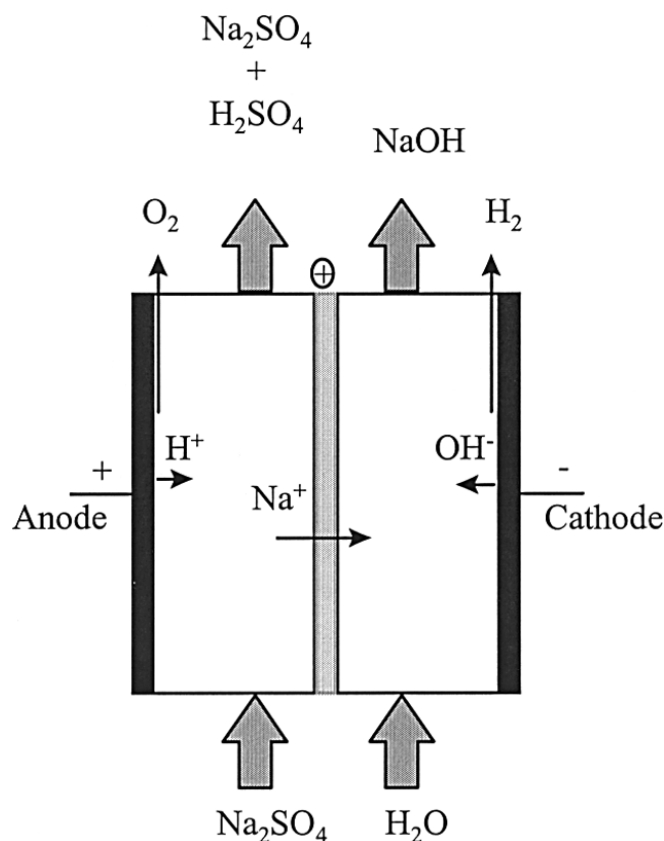


Figure 1. Simplified schematic of a single unit cell.

* Electrochemical Society Active Member.

** Electrochemical Society Student Member.

^c Present address: H Power Enterprises of Canada, Ville St-Laurent, Quebec, Canada H4R 1V8.

^d Present address: Technologies Novimage, Montreal, Quebec, Canada H3C 3R7.

^e Present address: Microelectronics Center, New Jersey Institute of Technology, Newark, NJ 07102, USA.

^z E-mail: fgirard@hpower.ca

sodium/sulfur batteries.¹¹ The NASICON abbreviation stands for sodium super ionic conductor. Its general formula is $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, where x ranges from 0 to 3. The ceramic with $x = 2$ was found to have the highest ionic conductivity. The structure of NASICON is essentially an assembly of unit cells composed of two Zr_2O_6 octahedra and three Si (or P) O_4 tetrahedra sharing oxygen atoms arranged in a rhombohedral structure. This arrangement leads to the formation of conduction channels in which the sodium ions are located. A three-dimensional path is formed by the intersection of the conduction channels. The size of these channels is such that sodium ions can circulate freely through them. As a result, this ceramic is highly selective to sodium. This property of NASICON was exploited by using it as a membrane in sodium-ion selective electrodes¹²⁻¹⁵ and, subsequently, in the splitting of sodium salts to their corresponding acid and base.⁷⁻¹⁰ However, the main problem with such membranes is their relatively high electrical resistance or low ionic conductivity at room temperature, $10^{-3} \Omega^{-1} \text{cm}^{-1}$.

To address this problem, we deposited this ceramic material on a suitable substrate in the form of a thin film using pulsed laser deposition (PLD). This technique employs a target of NASICON synthesized by conventional methods and placed facing a substrate. A laser beam is then focused on the target. The high energy density of the laser induces an evaporative explosion with ejection of material from the target, normal to its surface. The deposition can be performed on any substrate facing the target without any prior treatment. It has been demonstrated that thin films of NASICON having the same stoichiometry as the target can be deposited by this technique.¹⁶ In the latter study, a SiO_2/Si substrate was used. Recently, we reported the deposition of NASICON thin films on cation-selective polymeric membranes.¹⁷⁻¹⁹ The objective here was to prepare composite membranes which combine the low electrical resistance and high mechanical flexibility of polymeric membranes with the selectivity and resistance to fouling and to aggressive media of ceramic membranes.

This paper discusses the evaluation of composite membranes made of NASICON ceramic deposited on Raipore (RAI) 4010 cation-selective membranes. The composite membranes, designated as RAI-N, were incorporated in electrolytic cells used for the production of sodium hydroxide and sulfuric acid from sodium sulfate. The performance of the composite membrane is compared with the polymeric base membrane under similar operational conditions.

Experimental

Synthesis of the NASICON target.—The NASICON target was prepared by mixing powders of Na_3PO_4 and ZrSiO_4 in the required stoichiometric ratio. The mixture was then ground, pressed at 500 bar, and sintered at high temperature (1200°C) for 6 h.

Deposition of NASICON by pulsed laser deposition (PLD).—A NASICON target was installed facing a polymeric membrane substrate in the deposition chamber. A laser beam was focused on the target at various energy densities (from 0.7 to 2 J/cm²). The focused high energy caused the ejection of material from the target which deposited on the polymeric substrate. The deposition rate of material depended on the energy density of the laser beam. Typical rates ranged from 2×10^{-3} to 0.03 nm/pulse. The resulting thin films exhibited low roughness as verified by atomic force microscopy, except for a small number of fine particles, <0.1 μm, on the surface.¹⁶ Typically, the thickness of the ceramic layer was roughly 120 nm.

Electrochemical cells.—Two types of electrolysis cells were used in this work. The first (cell A), a hexagonal cell was supplied by Graver-Aqualytics. Current efficiency measurements were conducted using this cell, which can be operated under hydrodynamic conditions representative of industrial-scale systems. The width of the two electrode compartments was 1 mm and the membrane surface 27 cm². The electrodes were platinum disks having an area of 5.3 cm². The circulation of the solutions inside the cell was assured using a peristaltic pump. A flow rate of approximately 0.1 L/min was used, corresponding to a linear velocity inside the cell of about 4 cm/s.

A second, modular, two-compartment Plexiglas cell (cell B) was used for preliminary evaluation of membrane selectivity, resistance to fouling and durability. Each compartment contained approximately 13 mL of solution, continuously recirculated with a peristaltic pump. The working area of the membrane and the platinum electrodes was 1 cm². The distance between the electrodes and the membrane was 4 cm. The flow rate was 4.8 mL/min corresponding to a linear velocity of 0.02 cm/s.

Current efficiency measurements.—The current efficiency for the production of sodium hydroxide from sodium sulfate was measured using cell A incorporating the composite membrane or the RAI base membrane. The ceramic layer of the composite membrane faced either the cathode or the anode. The orientation of the ceramic layer is specifically mentioned for each type of experiment since, as determined later in the text, this parameter is of importance. The initial compositions of the anolyte and catholyte in typical electrolysis experiments were 1 M in Na_2SO_4 and 1 M in NaOH, respectively. The concentration should be higher for accurate simulation of the conditions used in industrial systems, but a higher temperature of operation would also be required since from an industrial point of view, the ohmic resistance of the system is lowered with a higher temperature. The anolyte was operated either in a batch or a simulated feed-and-bleed mode, while the catholyte was always operated in a simulated feed-and-bleed mode (water was added to the catholyte to maintain the concentration constant). When the anolyte was operated in a batch mode in cell A, the initial concentration of sodium sulfate in the anolyte was closer to saturation, at 1.5 M, in order to simulate more accurately the conditions used industrially (see results in Fig. 2). The simulated feed-and-bleed mode for the anolyte was performed using a large volume of solution to avoid having significant changes in the acidity of the anolyte during the experiment. In this case, the anolyte was maintained at 0.7 N in sulfuric acid and 1 M in sodium sulfate. The current density applied was 150 mA/cm² of electrode area. The voltage drop across the cell was monitored during the experiment. The concentrations of base and acid in the two compartments were measured using the titration technique.

Selectivity of the membrane for Na^+ over K^+ .—To evaluate the selectivity of the membrane for sodium over potassium ions, an electrolysis experiment was conducted using cell B in which the anolyte contained 0.5 N Na_2SO_4 and 0.5 N K_2SO_4 . The catholyte was 1 M in NaOH. The current density applied was 150 mA/cm². The membrane was oriented so that the ceramic layer faced the anolyte. Chemical analysis of the anolyte was conducted periodically to evaluate the K^+/Na^+ ratio.

Fouling experiments.—The composition of the anolyte and the catholyte were the same as for the current efficiency experiments except that a certain amount of fouling agent was added to the

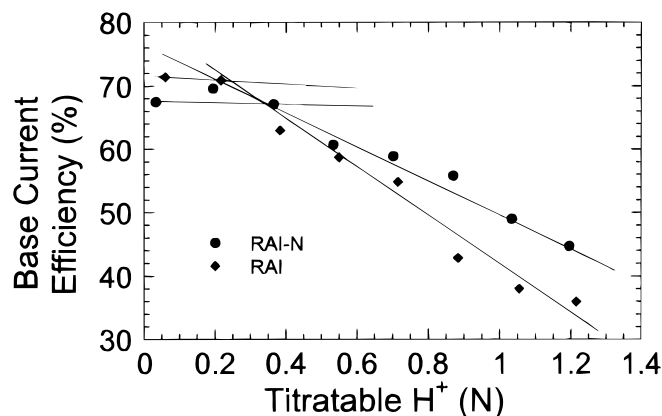


Figure 2. Base current efficiency curves of RAI polymeric membrane and RAI-N composite membrane for Na_2SO_4 splitting. $I = 150 \text{ mA/cm}^2$. Anolyte: 1.5 M Na_2SO_4 ; catholyte: 1 M NaOH.

anolyte. The fouling experiments were conducted using cell B. For the experiment with iron, sufficient ferrous sulfate was added to the anolyte to obtain a concentration of iron ions of 101 ppm. In the experiment involving calcium, sufficient CaSO_4 was added to the anolyte to obtain an initial concentration of calcium ion of 50 ppm. During the experiment, calcium sulfate was added to the solution to accelerate the fouling process. In the fouling experiment involving the magnesium ions, the anolyte initially contained 200 ppm of magnesium ion, added as magnesium sulfate. The current density applied to all systems was 150 mA/cm^2 . The membrane was oriented so that the ceramic layer faced the anolyte.

In all fouling experiments, the alkalinity of the catholyte was adjusted periodically to maintain alkalinity of 0.95-1.05 N. In the case of iron and calcium, the neutralization of the anolyte was conducted to a value of 0.6 N acid. The anolyte was neutralized to an acid concentration of 0.3 N during the magnesium experiment. The reason for this specific value of acidity is explained later.

Membrane durability.—Cell B incorporating a composite membrane was operated in a simulated feed-and-bleed mode in which the acidity and alkalinity were periodically adjusted to their initial values using sodium hydroxide and sulfuric acid, respectively. The durability experiment was conducted by maintaining an anolyte composition of 1 M Na_2SO_4 and 0.7 N H_2SO_4 and a catholyte composition of 1 M NaOH. The membrane was oriented with the ceramic layer facing the catholyte or the anolyte. The current density used was 150 mA/cm^2 . During these experiments, the voltage drop across the cell and the base current efficiency for the production of sodium hydroxide served as an indication of the state of the membrane.

Results and Discussion

Current efficiency.—In the preliminary experiments, we employed cell B to compare the performance of the composite membrane with the base RAI polymeric membrane.^{17,18} Even though the results obtained demonstrated a clear improvement in the current efficiency for the production of base for the cell incorporating the composite, as compared to the polymeric membrane, the geometry of the cell and the conditions under which it was operated do not reflect industrial-scale systems. In particular, the distance between the electrodes and the membrane was too large. In addition, the linear flows along the membrane and the electrodes were too low. For these reasons we reevaluated these membranes using a more appropriate cell, cell A, as described in the experimental section.

Batch Mode of Operation

Figure 2 compares the base current efficiency for the production of sodium hydroxide from sodium sulfate in electrolysis cell A incorporating (a) a RAI-N composite membrane with the ceramic layer (120 nm) facing the cathode, and (b) a RAI base membrane. In these experiments, the anolyte was operated in the batch mode and the catholyte in a simulated feed-and-bleed mode (see Experimental). As seen in Fig. 2, the current efficiency for the production of base is similar for both the composite membrane and the RAI cation-selective membrane up to an anolyte acidity of 0.7 N titratable H^+ . At higher acidity, from 0.7 to 1.2 N, the current efficiency of the composite membrane is superior to the one associated for the RAI base membrane. In Fig. 2, the current efficiency of the composite membrane declines with increasing acidity in the anolyte at a lower rate compared to the polymeric membrane. This suggests that the selectivity of the membranes to sodium over hydrogen ions declines with increasing acidity in the feed solution. This behavior is consistent with results obtained by Sujita *et al.*⁸ which show that, under the influence of an electric field, sodium ions in NASICON can be replaced by hydronium ions and a loss of selectivity occurs for the composite membrane. The current efficiency of the two membranes changes with the acidity of the anolyte according to the model proposed by Jörissen and Simmrock⁶ where the membrane shifts from an alkaline to an acidic state during the salt splitting process. The alkaline state is characterized by a quasi-constant current efficiency at low acidity. In the acidic state the current efficiency decreases in a linear fashion with the acid-

ity. In Fig. 2, the alkaline state is observed up to a concentration of 0.2 N for the polymeric membrane and up to 0.35 N for the composite membrane. In the acidic state, the selectivity of the composite membrane declines at a slower rate compared to the polymeric membrane indicating an improvement of selectivity for the composite.

The cells using the composite membrane showed a similar voltage drop (about 5 V) compared to the one using the unmodified RAI membrane. The ceramic film is thin enough so that its contribution to the membrane overall electrical resistance is very small compared to that of the polymer (~1%). Thus, in this respect, the modification of the polymeric membrane by the deposition of the thin ceramic film does not have a negative impact on energy consumption.

Feed-and-Bleed Mode of Operation

Table I compares the current efficiency, voltage drop, and energy consumption for the production of sodium hydroxide from sodium sulfate in an electrolysis cell, cell A, incorporating: (a) an RAI-N composite membrane with the ceramic layer (112 nm) facing the anode, (b) an RAI-N composite membrane with the ceramic layer (112 nm) facing the cathode, (c) an RAI base membrane, and (d) a Nafion 417 membrane used in other work.⁴ In these experiments, the anolyte and the catholyte were operated in a simulated feed-and-bleed mode (see Experimental). The values reported in the table represent an average of 8 to 11 measurements each. The voltage drop measured was the same for all RAI-based systems, demonstrating again that the deposition of a ceramic thin film and its orientation do not affect the electrical resistance of the polymeric membrane. The current efficiency of the composite membrane in both orientations was superior compared to that of the unmodified membrane. The best results were obtained with the RAI-N membrane oriented with the ceramic layer facing the catholyte (46.2% improvement in current efficiency). The other orientation of the composite membrane resulted in a 10.1% improvement in current efficiency compared to the unmodified RAI membrane. The reduced current efficiency in the latter case appears to be due to the ceramic layer of the composite membrane being attacked and partially solubilized by sulfuric acid. When compared to the Nafion 417 membrane, one can see that the composite membrane with the ceramic layer oriented toward the catholyte shows a comparable efficiency. A 78% current efficiency for the production of sodium hydroxide from sodium sulfate was reported using the Nafion 417 membrane⁴ compared to 70% for the ceramic-polymer composite membrane facing the cathode under similar conditions. When one compares the current efficiency of the membranes, RAI and composite, operated in either the batch or the feed-and-bleed mode, a different value is obtained. This difference between the two values can be explained by the different conditions of exposure to acidity during the experiments. In the batch mode, the acidity builds up gradually. At low acidity, the current efficiency is at its maximum and slowly decreases with the acidity increasing. The average efficiency determined at each acidity level is then strongly influenced by the initial values calculated at low acidity. When the system is operated in the feed-and-bleed mode, the acidity level is held constant throughout the experiment. The current efficiency in this case is more appropriate for the calculation of the energy consumption, since industrial systems are usually operated in this mode.

Table I. Comparison of the performance of RAI and RAI-N membranes in sodium sulfate splitting.

Membrane	Base current efficiency (%)	Voltage drop (V)	Energy requirement (kWh/kg NaOH)
RAI	48.5	4.9	7.13
RAI-N facing catholyte	70.9	4.9	4.70
RAI-N facing anolyte	53.4	4.9	6.00
Nafion 417 ^a	78		

^a From Ref. 4, value obtained under different conditions.

As a result of the improvement in current efficiency, the energy consumption was improved with the deposition of the NASICON thin film on RAI. When the ceramic layer faced the catholyte, the energy required to produce sodium hydroxide was 4.70 kWh/kg, an improvement of 34.1% compared to the RAI membrane. A higher energy consumption was cited for a freestanding RE-NASICON membrane¹⁰ at a lower current density ($<100 \text{ mA/cm}^2$). This means that a high electrode and membrane area would be required to achieve the same production rate as in our system or, alternatively a freestanding membrane having a thickness less than $1 \mu\text{m}$ would have to be fabricated to achieve the same objective. In addition, it was reported that freestanding NASICON membranes are attacked and degraded by sulfuric acid starting at a concentration of about 0.25 N.⁸ The same problem was encountered with our membranes when the ceramic layer faced the anolyte. The cell incorporating an RAI-N membrane with the ceramic layer facing the anode had an energy requirement of 6.0 kWh/kg of NaOH representing a modest improvement of 15.8% compared to the unmodified RAI membrane. It appears that approximately 40% of the ceramic material is dissolved when the membrane is exposed to sulfuric acid.¹⁸ After the initial loss, the amount of NASICON remaining on the membrane stayed constant suggesting that only some soluble phase existing in the ceramic was attacked. When a second batch electrolysis experiment was performed with a composite membrane which had been previously used, the current efficiency for the production of sodium hydroxide was lower in the case of an RAI-N membrane with the ceramic layer facing the anolyte. These results can be explained by the longer exposure to an acid concentration sufficient to attack the ceramic. We found that this problem can be addressed by orienting the ceramic layer of the composite membrane toward the catholyte since NASICON is much more chemically stable under alkaline conditions. Another parameter, which affects the current efficiency, is the thickness of the ceramic layer. Results on this are presented elsewhere.²⁰

Selectivity for sodium over potassium.—To study the selectivity of the composite membrane for sodium over potassium ions, an electrolysis experiment was conducted with a modified and unmodified membranes in which the anolyte was filled with sodium and potassium sulfate at a 1:1 molar ratio. The sodium and potassium levels in the anolyte were analyzed periodically. The concentration of both ions in the anolyte decreased during the experiment since they were transferred from the anolyte to the catholyte. Figure 3 presents the change in the K^+/Na^+ molar ratio in the anolyte over the course of the experiment. A molar ratio of 1 would suggest that both ions are transferred at the same rate while a ratio higher than 1 would indicate that sodium ions travel through the membrane at a faster rate than potassium ions. Finally, if the ratio was smaller than 1, it would sug-

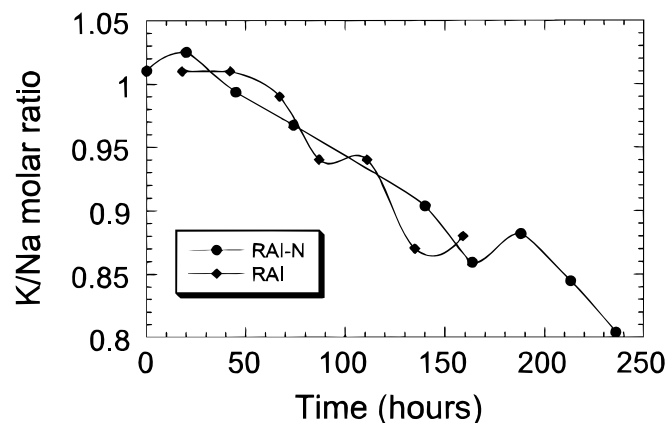


Figure 3. Variation of K^+/Na^+ ratio in the anolyte during the electrolysis of 1:1 $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$ mixture for RAI and RAI-N membranes. $I = 150 \text{ mA/cm}^2$. Initial anolyte concentration: 0.5 N of each salt; catholyte: 1 M NaOH.

gest that potassium ions are transferred preferentially to sodium ions. The molar ratio obtained during the experiment is mostly below 1 for both membranes. This result is not surprising in the case of the RAI polymeric membrane since conventional cation-selective membranes demonstrate a 2:1 preference for potassium over sodium ions.^{21,22} A similar selectivity was obtained for the composite membrane. The ionic mobility in dilute solution of potassium ions is greater than sodium ions, 7.62×10^{-4} vs. $5.19 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$.²¹ Consequently, potassium ions arrive at the surface of the membrane more rapidly and are able to be transferred preferentially to sodium ions to the catholyte. The mobility of potassium ions across a cation-selective membrane such as Nafion is also higher than that of sodium ions, 4.3×10^{-6} vs. $3.24 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$.²² Our results are consistent with previous reports demonstrating that potassium ions were able to cross a freestanding NASICON-based membrane at an appreciable rate compared to sodium ions under the influence of an electric field.^{9,10}

Resistance of the composite membrane to fouling.—Cation-selective membranes tend to foul when multivalent metal ions such as those of iron, magnesium, and calcium are present in solution. The fouling of a cation-selective membrane occurs as a result of the precipitation of insoluble hydroxide salts of the multivalent cations inside the membrane.⁶ The fouling is reflected by an increase in the voltage drop across the membrane and the overall cell potential. In three separate experiments, iron, calcium, and magnesium were added to the anolyte, in exaggerated quantities compared to what is found in most pulp and paper industrial effluents, during the electrolysis of sodium sulfate, in order to study the resistance to fouling of the composite membrane. Experiments with the RAI membrane were conducted in parallel for comparison. The results of the fouling experiment involving iron are presented in Table II. In these preliminary experiments, the ceramic layer of the RAI-N membrane faced the anolyte.

In order to study the effect of ferric ion on the fouling of the membrane, 101 ppm of ferric ion were added to the anolyte in the ferric sulfate form. In these experiments, the RAI membrane fouled after 4 days of continuous operation in the batch mode. A reddish-brown film formed on its surface, facing the anolyte. The layer thickened with time and eventually expanded through the membrane resulting in fouling. In this case, pretreatment of the solution would be needed to operate with this membrane. On the other hand, the cell incorporating the composite membrane was continuously operated for 25 days without the membrane being fouled. A film similar to that observed for the RAI membrane formed at the surface of the composite membrane in the beginning of the experiment. However, the thickness of this film increased to a certain point, beyond which it stopped expanding. Evidence for this is provided by the fact that the concentration of iron in the anolyte initially declined to 42 to 45 ppm (film formation) but then remained the same for the duration

Table II. Iron content analysis of the anolyte and catholyte during the electrolysis of sodium sulfate containing iron sulfate for RAI-N composite membrane.

Time (days)	[Acid] in anolyte (N)	$[\text{Fe}^{3+}]$ in anolyte (ppm) ^a	$[\text{Fe}^{3+}]$ in catholyte (ppm)
2	0.201	42.1	0.3
6	0.382	43.5	<DL ^b
8	0.477	43.3	<DL ^b
10	0.495	43.3	<DL ^b
13	0.616	44.8	0.3
17	0.753	44.0	<DL ^b
21	0.878	45.3	<DL ^b
25	0.999	43.7	<DL ^b

^a Initial concentration = 101 ppm of ferric ion as FeSO_4 .

^b <DL: Below detection limit.

of the experiment (Table II). It appears that the ceramic layer blocked the penetration of ferric ions into the polymeric membrane, preventing its fouling. This conclusion is supported by the fact that no ferric ions were detected in the catholyte in the duration of the experiment (Table II). The formation of a hydroxide or oxide film on the surface of the membrane facing the anolyte at the beginning of the experiment can be explained through a model for cation-selective membranes developed by Jörissen and Simmrock.⁶ According to this model, at high sodium hydroxide concentrations in the catholyte and low concentrations of acid in the anolyte, the cation-selective membrane is in the alkaline state. This is because, under these conditions, the flux of hydroxide ions back-diffusing from the catholyte to the anolyte under the influence of the electric field exceeds the flux of hydrogen ions crossing the membrane from the anolyte to the catholyte. As a result of this situation, the cation-selective membrane is in the alkaline state through its entire thickness and an alkaline boundary layer is developed on the anolyte side of the membrane. Therefore, multivalent metal ions such those of iron for which the solubility product constants of their hydroxide are relatively low have a very high chance of precipitating out in the boundary layer. Since ferric hydroxide ($K_{sp} = 2.64 \times 10^{-39}$), and in particular ferric oxide are not very soluble, they remained on the surface of the membrane even when the anolyte became acidic. The model for the alkaline state of a membrane seems also to apply to ceramic-based membranes for which the back-diffusion of hydroxide ions was reported to be possible.¹⁰

When the membranes were exposed to calcium or magnesium, neither membrane fouled. However, during the experiment using magnesium, a white cloudy precipitate was formed on the anolyte side of the membranes in the beginning of the experiment while the anolyte was still neutral or slightly acidic. This precipitate was obviously magnesium hydroxide. This observation suggested that the cation-selective membranes were in the alkaline state.⁶ Consequently, magnesium ions precipitated as insoluble hydroxide salts at the anolyte-membrane interface. As the acidity built up, the membranes shifted from the alkaline to the acidic state and the magnesium hydroxide dissolved. At 0.3 N acid, we observed that the white cloudy precipitate disappeared completely in the case of both membranes, modified and unmodified. Unfortunately membranes with the ceramic facing the catholyte do not prevent fouling.

Water transport across the composite membrane.—Water transport is an important parameter for electromembrane systems. The amount of water transferred with the cation is reflected in the concentration transport number. This number is the percentage by weight of the cation transferred relative to the total weight, cation plus water, of material transferred. A water balance was carried out for all electrolysis experiments conducted. The average concentration transport number obtained was found to be between 10 and 15%. This number is similar to the concentration transport number obtained for the RAI membrane alone. This corresponds to the transfer of 4-8 mol of water per mol of sodium. This compares well with the number of water molecules in the hydration sphere of sodium. The ceramic layer does not affect the water transport properties of the membrane. This suggests that NASICON is able to allow the passage of water molecules and/or hydrated ions. These results are in line with the observation that some rare-earth based NASICON freestanding membranes expand by 0.7% because of the hydration of the silicate backbone.¹⁰

Durability of the composite membrane.—A study of the durability of the composite membrane with the ceramic layer facing the catholyte was conducted using cell B. In this experiment, the anolyte was 0.7 N in sulfuric acid and 1 M in sodium sulfate. The anolyte was maintained at 1 M sodium hydroxide. The acidity and alkalinity were periodically adjusted to these levels by neutralization. Figure 4 presents the current efficiency vs. time over the course of the durability experiment. As seen in this figure, the current efficiency declined from 70 to 56% over the first 300 h and subsequently

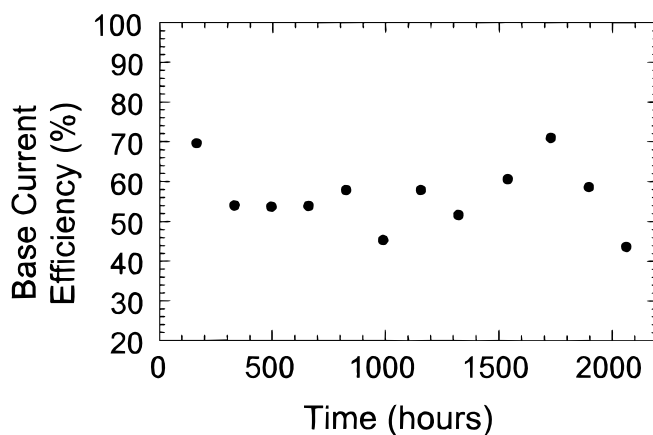


Figure 4. Variation of the base current efficiency for RAI-N composite membrane with time during the durability experiment in sodium sulfate splitting with the ceramic layer facing the catholyte. $I = 150 \text{ mA/cm}^2$. Anolyte: 0.7 N H_2SO_4 and 1 M Na_2SO_4 ; catholyte: 1 M NaOH.

remained relatively constant over the remaining 1900 h. A similar experiment with the ceramic layer facing the anode was performed (not shown). In the latter experiment, the current efficiency dropped continuously to reach an approximate value of 34% within 200 h. As previously discussed, this is likely to be due to the partial solubilization of the ceramic layer by acid.

Conclusion

Using PLD, a new composite cation-selective membrane was prepared by depositing a sodium-ion selective ceramic thin film on a polymeric cation-selective membrane. The resulting membrane showed an improved current efficiency for sodium hydroxide and sulfuric acid production from sodium sulfate and a remarkable resistance to fouling by iron compared to the unmodified polymer membrane. The ceramic layer of the composite membrane did not affect the water transport properties of the base polymeric membrane or its selectivity to potassium over sodium. The lower electrical resistance of the composite membrane compared to freestanding ceramic membranes resulted in lower energy requirements for the production of sodium hydroxide and sulfuric acid from sodium sulfate.

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