

NOVEL NASICON-POLYMER COMPOSITE MEMBRANE FOR ELECTRICALLY DRIVEN PROCESSES: EFFECT OF CERAMIC THICKNESS ON CURRENT EFFICIENCY

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ABSTRACT

We have studied the effect of thickness and of the technique of deposition used for thin films of NASICON ($\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, $0 \leq x \leq 3$) on a commercial cation-selective polymeric membrane on the base current efficiency. It was found that when general coverage of the polymeric substrate is obtained, the NASICON film improves the salt splitting behaviour of the polymeric membrane even when localized surface imperfections are present. The mechanical properties of the NASICON film were observed to affect the base current efficiency (BCE) more than film morphology or chemical composition. The study showed that the BCE of an electrolysis cell does not differ significantly if the composite membrane is made by pulsed laser deposition (PLD) or by sputtering. In terms of current efficiency, the optimal NASICON thickness was found to be in the 70-100 nm range for the salt splitting conditions investigated.

INTRODUCTION

A cation-selective ceramic-polymer composite membrane has been proposed for chemical separation and regeneration of chemicals (1). Processes such as electrolysis and bipolar membrane electrodialysis employing composite membranes could be used to recover sodium hydroxide and sulphuric acid from the sodium sulphate by-product generated by chlorine dioxide generators in kraft pulp mills (2). To be economically interesting, the electromembrane process must display high energy efficiency and require minimal maintenance during an extended useful lifetime. The selectivity of a membrane is a key property for achieving these goals because it acts on two levels: (i) selectivity of the membrane for Na^+ ions over H^+ ions directly affects energy efficiency, and (ii) selectivity over multivalent ions delays fouling and increases the lifetime of the membrane. Fouling occurs by the formation of insoluble hydroxide salts inside the membrane which may increase the electrical resistance of the membrane thereby increasing energy requirements and leading to premature replacement of the membrane.

At present, electromembrane systems primarily use ion-selective membranes that are entirely polymeric. Two desirable features of polymers are their low electrical resistance and their mechanical flexibility. Their drawbacks are that their selectivity to alkali metal

ions declines with increasing acid concentration in the feed compartment or high alkali concentration in the base compartment (2,3) and that they are sensitive to oxidation at high temperatures. Ceramic membranes provide enhanced current efficiencies as compared to conventional polymeric membranes and can operate at higher temperatures than polymers without being damaged. The thickness required for self-supporting ceramic membranes leads to high resistance and increases the energy consumption to unacceptable levels.

The proposed composite membrane consists of a thin film of NASICON ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, $0 \leq x \leq 3$) deposited on a cation-selective polymeric membrane. We have shown (4) that the presence of a NASICON thin film on a polymer membrane increases current efficiency and prevents fouling. The composite membrane combines the advantages of both polymer (mechanical flexibility and low electrical resistance) and ceramic (Na^+/H^+ selectivity and low multivalent ion fouling rates) (4). In the initial phase of the study, the composite membranes were produced by pulsed laser deposition (PLD)(5) and their performance showed an improvement over that of unmodified polymer membranes (4). Membranes have also been deposited using the more conventional RF magnetron sputtering technique. The objectives of the present study were twofold: (i) determine if there are changes in the performance of the membrane when a different deposition technique is used, and (ii) determine the optimal film thickness for the intended applications.

EXPERIMENTAL

The substrates were cation-selective fluorocarbon polymeric membranes (Pall Corp., NY). A small sample of silicon nitride on Si was coated alongside the polymeric substrate for thickness measurement purposes. The NASICON thin films were deposited by PLD and RF magnetron sputtering from bulk NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) targets. The target fabrication and experimental set-up for PLD have been described elsewhere (5,6). The beam of an excimer laser (KrF, 248 nm) was focused on the rotating NASICON target to an elliptic spot size of 2.2 mm^2 . The energy density was adjusted to 0.6 J/cm^2 at a laser repetition rate of 30 Hz. RF magnetron sputtering was performed at 75 W under 5 mTorr Ar pressure. For the thickness study, two series of NASICON films were deposited at nominal thickness ranging from 40 to 450 nm.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab MKII, calibrated with the Ag $3d_{5/2}$ line at -368.3 eV . Non-monochromatized Mg $K\alpha$ (1256.3 eV) radiation from a dual anode was used as the X-ray source. The source was generally operated at 15 kV, 20 mA, and was sometimes used at 12 kV, 10 mA to prevent radiation damage to the polymeric membrane. Relative atomic compositions were calculated from low resolution survey scans using the empirical sensitivity factors published by Briggs et Seah (7). Scanning Electron Microscopy (SEM) images were taken of the composite membranes before and after electrochemical evaluation. Image analysis of SEM micrographs was performed using ImageTool version 2.00, a shareware from the University of Texas.

The performance of the composite membrane for electrolysis was assessed in a Hexagonal Stack Cell (HSC) (Graver-AQUALYTICS, NJ). A simplified schematic of

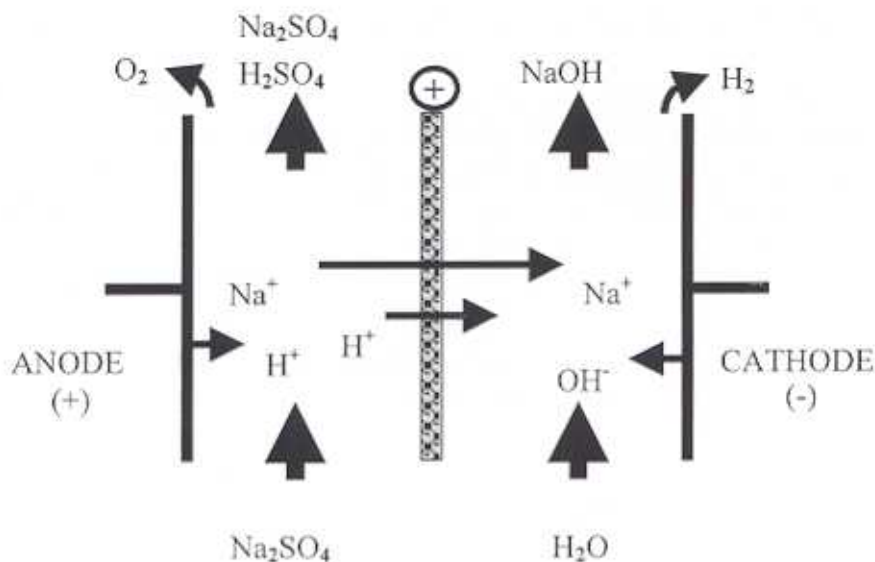


Fig. 1. Simplified schematic illustrating the principle of salt splitting using electrolysis.

electrolysis is presented in Fig. 1. The current density was maintained at 150 mA/cm^2 . The anolyte was a solution of $1 \text{ M Na}_2\text{SO}_4$ and $0.7 \text{ N H}_2\text{SO}_4$ and the catholyte was a solution of 1 M NaOH . The HSC was run in a simulated Feed-and-Bleed mode at room temperature, that is, the volume of electrolyte compartments was sufficiently large to avoid significant changes in concentrations over time. Acid and base concentrations were determined using titration. Current efficiency is defined as the fraction of the current consumed for useful work (in this case NaOH production). The Base Current Efficiency (BCE) is calculated as the ratio of the number of equivalents of Na^+ ions transferred across the membrane over the theoretical (Faraday's law) number of equivalents of Na^+ transferred for a known charge passed between the two electrodes.

The long-term performance of the composite membrane was also evaluated. The cell used for this experiment was a two-compartment Plexiglas cell requiring a working membrane area of 1 cm^2 . The electrolytes and applied current density were the same as described above. The membrane was positioned with the NASICON film facing the catholyte. Sampling and concentration adjustments were performed weekly for a period of 284 days.

RESULTS AND DISCUSSION

Characterization of as-deposited films

The as-deposited NASICON films and polymeric substrate material were examined by SEM and XPS. SEM micrographs showed that the polymeric substrate had pores which averaged $0.01 \mu\text{m}^2$ in diameter and were randomly distributed. The polymer also displayed some smooth texturing on a larger scale. The as-deposited films showed good overall coverage of the substrate, masking the pores completely, but followed the texture of the polymer. Very few film surface defects were present and these were in the form of pinholes. The samples deposited by PLD were rougher than the sputtered samples and

had particles on their surface. These particles are inherent to the PLD process and increase in size and number with increasing thickness (8).

Evaluation of the chemical composition of the films by XPS showed good transfer of stoichiometry from the target to the sample by either PLD or sputtering. It has already been observed that NASICON thin films deposited on a cation-selective membrane are depleted in sodium at the surface and enriched in Na at the film/substrate interface (5). The composition did not vary significantly for the different film thickness deposited. The only significant difference in the composition of the films deposited by the two techniques is that there is depletion in phosphorus at the surface of the PLD samples whereas there is enrichment in phosphorus at the surface of the sputtered samples. Table I presents the relative atomic compositions of typical NASICON films on polymer deposited by both techniques.

Table I. Relative atomic compositions of NASICON thin films deposited on the polymeric membrane.

Element	PLD (at. %)	RF Magnetron Sputtering (at. %)
Na	<1	<1
O	65	67
Zr	15	11
P	5	11
Si	15	11

Electrochemical tests

The effect of NASICON thickness and deposition technique on the base current efficiency is shown in Fig. 2. Membranes deposited by sputtering and PLD did not show a significant difference in BCE for a given thickness. Both curves show a maximum BCE around 70-100 nm and then the BCE steadily declines until it reaches a plateau at about 44%. For ceramic films thinner than 70 nm deposited by PLD, incomplete coverage of the substrate, as confirmed by fluorinated carbon groups detected by XPS, produced a BCE similar to the uncoated membrane. For the corresponding sputtered film, the very low BCE obtained can only be explained by the probable presence of a small rupture in the membrane causing the partial mixing of the anolyte and catholyte solutions thereby neutralizing some of the hydroxide ions produced in the catholyte. This is supported by the observed decrease in OH^- concentration with time instead of the expected increase.

For the remainder of the sample set, the NASICON films provided overall coverage of the substrate and the value of the BCE is probably determined primarily by the area of the polymer substrate exposed to the catholyte due to localized surface defects in the NASICON film. Portions of the membrane where the NASICON coating is removed represent areas where H^+ ions can cross to the catholyte compartment at higher fluxes because the polymer is not as Na^+/H^+ selective as NASICON. This decreases the total Na^+ ions transferred and thus the BCE, but does not completely eliminate the beneficial effect of the NASICON film (the BCE is still 4 % higher than for the uncoated membrane).

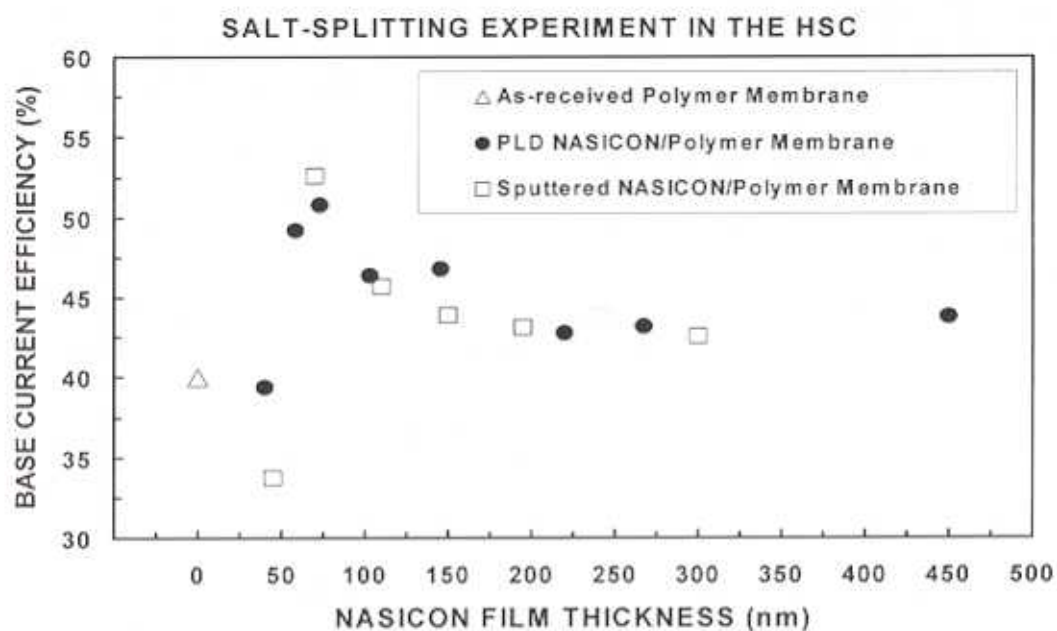


Fig. 2. Effect of NASICON thickness and deposition technique on base current efficiency.

Supporting evidence to this hypothesis comes from microscopic observations. The membranes examined by SEM after electrolysis experiments revealed that cracks had formed in the coating and that new pinholes with smooth edges had been created. Quantification of the images using image analysis was attempted but was difficult due to the minimal contrast between the coating and the substrate of some samples. It was estimated that the average pinhole size was $0.02 \pm 0.02 \mu\text{m}^2$, thus sufficiently large to allow ionic transfer. The high BCE values were observed for the films that had defects occupying less than 1% of the surface area and the maximum BCE was obtained for the sample for which no defects could be seen by microscopy. If the surface defects occupied more than 1% of the total area, then a drop in BCE from the maximum was observed, although the BCE was still 4% higher than for the polymeric membrane alone. The drop in BCE indicates that the increased Na^+/H^+ selectivity provided by the NASICON film tended toward that of the polymeric substrate.

The defects appear to be caused by mechanical action as well as by chemical action. PLD films thicker than $>100 \text{ nm}$ showed a more disrupted surface than the thinner ones, with ruptured film edges overlapping in certain areas. Differential expansion of the coating and the polymer upon immersion in solution combined with the mechanical stresses linked to the installation of the membrane in the cell, and operation under flow are factors that could cause the separation of the coating from the polymer. For sputtered samples, mechanical removal of significant portions of the film had occurred, indicating a less well-adhered film as compared to the PLD samples.

The smooth-edged pinholes are attributed to localized chemical dissolution of the NASICON film. XPS analysis of the NASICON films after salt-splitting experiments provided the following information. The relative concentrations of P and O decreased with respect to the other elements, indicating that there may be loss of phosphorus in the

form of phosphates. Zr decreased relatively to Si, and this decrease was more pronounced for the sputtered samples. The initial enrichment in P of the sputtered samples did not lead to retention of more phosphorus after electrolysis.

The observed localized dissolution of the film does not spread rapidly, as very good BCE results (~54%) were obtained for over 200 days of operation with the PLD-deposited NASICON film facing the catholyte (Fig. 3). SEM and XPS analysis of the sample after the durability showed that some of the NASICON film remained on the surface although it was thinned and cracked in most areas. A similar study will be undertaken for a sputtered NASICON film.

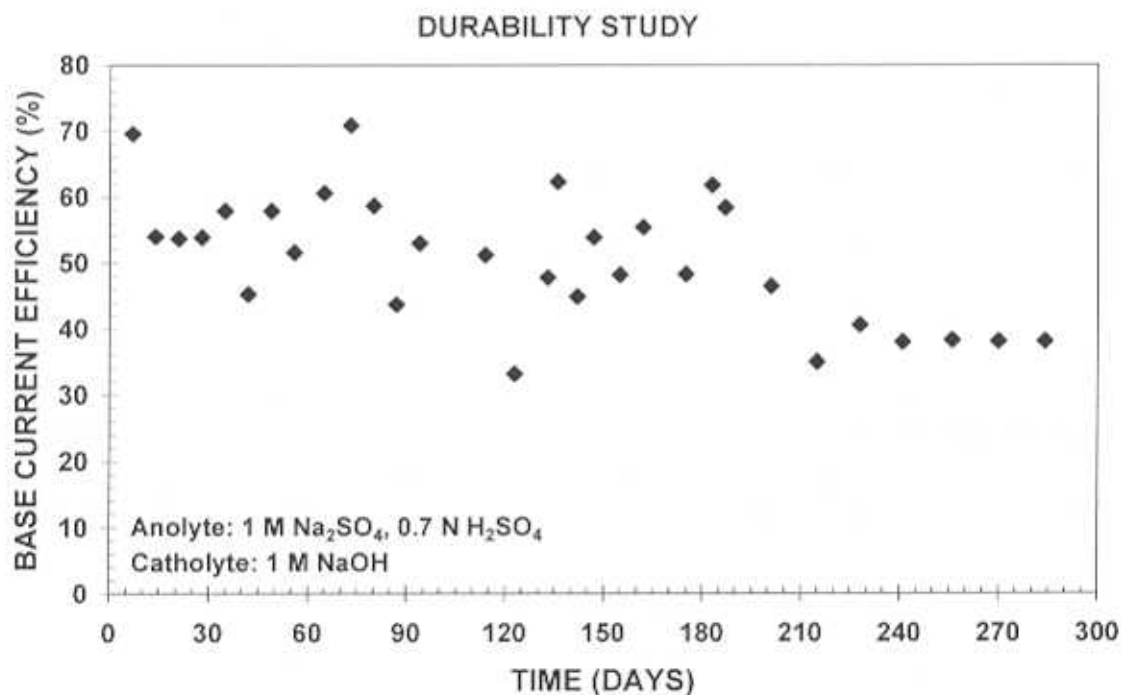


Fig. 3. Durability study for the composite membrane with the NASICON facing the catholyte.

CONCLUSIONS

- (i) NASICON/polymer composite membranes improve the current efficiency for the production of sodium hydroxide from sodium sulphate in an electrolysis cell as compared to the polymer membrane alone.
- (ii) Provided overall coverage of the polymeric substrate, the NASICON film improves the salt splitting performance of the polymeric membrane even when localized imperfections are present in the film. For optimal results, imperfections (i.e. cracks, pinholes) should occupy less than 1% of the surface.
- (iii) The mechanical properties (e.g. adhesion) of the NASICON film appear to play a more important role than morphology or chemical composition in the resulting performance.
- (iv) The base current efficiency (BCE) of an electrolysis cell with a PLD-deposited composite membrane is not significantly different from the BCE of a cell with a composite membrane made by sputtering.

- (v) In terms of current efficiency, the optimal NASICON thickness is in the 70-100 nm range for the salt splitting conditions investigated.
- (vi) The composite membrane is able to produce a base current efficiency for the hexagonal stack cell of ~54% for at least 200 days of continuous operation.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada and the Pulp and Paper Research Institute of Canada (PAPRICAN). Dr. F. Girard and Dr. R. Izquierdo are thanked for fruitful discussions. Mr. E. Quenneville and Mr. P.-Y. Wong are thanked for their help with the experimental aspects of PLD and electrochemical testing.

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