

# Pulsed Laser Deposition of NASICON Thin Films for the Fabrication of Ion Selective Membranes

R. Izquierdo,<sup>a,\*</sup> E. Quenneville, D. Trigylidas, F. Girard,<sup>a,b</sup> M. Meunier,<sup>\*\*</sup> D. Ivanov,<sup>\*\*c</sup> M. Paleologou,<sup>\*\*b</sup> and A. Yelon<sup>\*\*</sup>

Group de Recherche en Physique et Technologie des Couches Minces (GCM) and Département de Génie Physique, Ecole Polytechnique de Montréal, Montréal, Québec, Canada H3C 3A7

## ABSTRACT

Pulsed laser deposition is used to deposit thin films of Na superionic conductor (NASICON). The resulting thin films are good ionic conductors with resistivities between  $3 \times 10^3$  and  $5 \times 10^4 \Omega \text{ cm}$  at room temperature depending on the deposition conditions. By depositing these films on Raipore cation-selective membranes, composite membranes can be fabricated. The cumulative current efficiency of these membranes for the production of sodium hydroxide from sodium sulfate using electrolysis is improved by 23%. In addition, the composite membranes presented a higher resistance to fouling by multivalent cations than the polymeric membranes.

## Introduction

Ion selective membranes are used in various applications in the biological, medical, chemical, pulp and paper, and other industries. Their use is in electrolysis and bipolar membrane electro dialysis for splitting salts into their component acid and base.<sup>1</sup> Polymeric or ceramic membranes can be used, each one having its advantages and drawbacks. Large area polymeric membranes can be manufactured and used to build leak-free systems. However, these polymeric membranes present problems of selectivity and fouling, which reduce efficiency and life. Ceramic membranes do not present these problems but, because of the thickness necessary for mechanical stability, they usually have high resistance. It is usually advantageous to combine the two types of material in a composite membrane which may have the advantages of both. One way to do this is to deposit a thin film of ceramic on a polymeric membrane. The polymeric membrane may be any of the existing ion selective materials such as Nafion<sup>®</sup> or Raipore<sup>®</sup>. An appropriate candidate for the ceramic material for Na salt splitting is NASICON. NASICON is a ceramic formed by a solid solution of  $\text{Na}_x\text{Zr}_2(\text{Si}_x\text{P}_{3-x}\text{O}_{10})_2$  and  $\text{Na}_x\text{Zr}_2(\text{SiO}_3)_2$  of average composition  $\text{Na}_x\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{10}$ , where  $x$  varies between 0 and 3. As indicated by its name, NASICON has a high ionic conductivity which depends on the value of  $x$ , and is maximal for  $x = 2$ .<sup>2</sup> Relatively thick NASICON films ( $>25 \mu\text{m}$ ) have been used as sodium selective membranes for sodium sulfate splitting.<sup>3</sup> However the use of thin films ( $<1 \mu\text{m}$ ) has not been reported.

Because of their complex stoichiometry, it is difficult to deposit NASICON thin films by conventional evaporation or sputtering techniques. Thin films of NASICON have been deposited using the sol-gel technique.<sup>4,5</sup> However, this process requires high temperature annealing ( $>700^\circ\text{C}$ ) which makes it unsuitable for deposition on polymers. Recently pulsed laser deposition (PLD) has emerged as a more suitable technique for deposition of ceramics with complex stoichiometry, such as high  $T_c$  superconducting oxides.<sup>6</sup> This technique is suitable for the deposition of superionic ceramics as well.<sup>7</sup>

## Experimental

In PLD the optical beam of a pulsed laser is focused at the surface of a target of the material which we wish to deposit as a thin film. The very high energy density impinging on the target induces an evaporative explosion, with ejection, normal to the surface, of material from the target. Because of the extremely high rate of temperature elevation, this process leads to a congruent evaporation of the target. If we place a substrate facing the target, deposition of a thin film occurs. Deposition can be performed in vacuum or using a reactive gas atmosphere.

The experimental setup used here has been described in detail elsewhere.<sup>7</sup> Briefly, the laser beam from a KrF excimer laser ( $\lambda = 248 \text{ nm}$ ) was focused on an elliptic spot with an area of 1 to  $2 \text{ mm}^2$ . The energy density incident on the target was controlled by attenuating the incoming laser beam. The laser repetition rate was 30 Hz.

The target-to-sample distance was varied from 5.5 to 10.5 cm, and samples were at room temperature.

NASICON targets were prepared from a mixture of  $\text{ZrSiO}_4$  and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  powders, pressed at 500 bar and sintered at  $1200^\circ\text{C}$  for at least 6 h. Deposition was done on Raipore R-4010 cation-selective polymeric membranes. The area of the membrane was varied from  $3 \times 3$  to  $7 \times 7 \text{ cm}^2$ . Some deposits were made on  $\text{Si}_3\text{N}_4/\text{Si}$  substrates to allow electrical measurement up to  $400^\circ\text{C}$ .

Film composition was measured by x-ray photoelectron spectroscopy (XPS). The film thickness was measured using a Dektak profilometer. The crystallography of the deposited films was evaluated using x-ray diffraction (XRD). The morphology was studied by scanning electron microscopy (SEM). Electrical characterization was carried out using ac and dc methods. Resistivity measurements were performed by ac impedance using a lock-in amplifier coupled with a potentiostat-galvanostat. The frequency range was from 0.01 Hz to 100 kHz. The measurements were done between two platinum electrodes,  $1.5 \times 6 \text{ mm}$  spaced by 1.5 mm, deposited by magnetron sputtering. The resistivity was evaluated from the high frequency intercept of the real-axis in the Nyquist plot. Efficiency and dc polarization measurements were made in a cell consisting of two Pt covered electrodes, two electrolyte compartments, and a  $1 \text{ cm}^2$  cation selective membrane separating these compartments. The current efficiency of the composite membrane was measured from the production of NaOH from the electrolysis of sodium sulfate. When a voltage is applied between the two electrodes, the sodium ions migrate through the membrane toward the negative electrode. The initial concentration of  $\text{Na}_2\text{SO}_4$  in the anolyte compartment was 1 M. NaOH was present in the catholyte compartment with an initial concentration of 1 M. The acid and base concentrations in the catholyte and anolyte compartments were measured by titration during the experiment.

## Results and Discussion

A main advantage of PLD is its ability to transfer stoichiometry from target to substrate, even for complex materials. However, this is not always the case. Even if the evaporation is congruent, the difference in sticking coefficients from different species, and the formation of volatile compounds during the flight from target to substrate may lead to nonstoichiometric deposition.<sup>8</sup>

We have reported that target stoichiometry is preserved when NASICON compounds are deposited on Si or  $\text{Si}_3\text{N}_4/\text{Si}$  substrates.<sup>7</sup> However, XPS measurements of the composition of films deposited on Raipore substrates show very small or even zero Na content

Table I. Composition of the surface of NASICON thin films deposited on: Raipore fresh membrane, Raipore membrane which was dipped in a  $\text{Na}_2\text{SO}_4$  solution, and  $\text{Si}_3\text{N}_4/\text{Si}$ .

	NASICON film on fresh Raipore (at.%)	NASICON film on modified Raipore (at.%)	NASICON film on $\text{Si}_3\text{N}_4/\text{Si}$ (at.%)
Zr	13	11	7
O	70	62	60
P	3	3	5
Na	1	15	21
Si	12	9	8

\* Electrochemical Society Student Member.

\*\* Electrochemical Society Active Member.

<sup>a</sup> Present address: Technologies Novimage, Montréal, Québec, Canada H3L 3R7.

<sup>b</sup> Present address: Pulp and Paper Research Institute of Canada, Pithou-Claire, Québec, Canada H9R 3J9.

<sup>c</sup> Present address: Microelectronics Center, New Jersey Institute of Technology, Newark, New Jersey 07102, USA.



at the surface of the films. In Table I we show the composition of NASICON films deposited on  $\text{Si}_3\text{N}_4/\text{Si}$  and Raipore substrates placed side-by-side in the processing chamber. Since Na is present in the film deposited on the  $\text{Si}_3\text{N}_4/\text{Si}$  substrate, we exclude the formation of volatile compounds as the cause of the Na depletion. After the deposition of the first few monolayers, further deposition takes place on a ceramic in both cases. Thus, we do not expect that the sticking coefficient difference could explain the Na depletion for thick films. When the Raipore membrane is dipped into a  $\text{Na}_2\text{SO}_4$  solution for a few hours, the composition of the Raipore surface is greatly modified. If the deposition is done on such a modified membrane the Na depletion is largely reduced (see Table I). Therefore, we suppose that Na diffusion into the polymer is the cause of depletion of Na from the ceramic deposited on a fresh Raipore membrane. Similar behavior is observed when NASICON films are deposited on  $\text{SiO}_2/\text{Si}$  substrates. In this case, elastic recoil detection (ERD) measurements show that Na concentration increases in the interior of the ceramic film. Despite the Na depletion, the ceramic film-Raipore composite membranes show excellent behavior as we show below.

The deposition rate may vary widely with various deposition parameters such as energy density, target to substrate distance, etc. Deposition rates ranging from  $2 \times 10^{-3}$  to  $0.03$  nm/pulse were obtained with a target-to-substrate distance of 5.5 cm and energy densities ranging from 0.7 to  $2$   $\text{J}/\text{cm}^2$ . This range is determined by the choice of deposition parameters, and does not represent the limits of deposition rates. Using a repetition rate of 30 Hz, the deposition of 100 nm, chosen as an appropriate thickness for the fabrication of a membrane, takes from 2 to 30 min, depending on deposition conditions. This value compares well with other techniques such as sputtering.

The energy density also has a major influence on the surface morphology of the deposited films. In Fig. 1, we show a micrograph of the surface of a NASICON film deposited on a Raipore membrane at  $0.72$   $\text{J}/\text{cm}^2$ . The surface is relatively smooth, with a small number of particles. For films deposited at higher energy density the number of particles and their size increase. An example of this is shown in Fig. 2, where the NASICON film was deposited at  $1.5$   $\text{J}/\text{cm}^2$ . The presence of particles can lead to the formation of pinholes which reduce the efficiency of the composite membrane. However, their relative area is small and, as seen later, they do not preclude the good operation of the composite membrane.

XRD measurements were undertaken to study the crystallographic state of the deposited films. Films deposited at medium and low energy density (below  $1.0$   $\text{J}/\text{cm}^2$ ) are amorphous as shown by the absence of characteristic peaks in XRD spectra (Fig. 3b). At higher energy density ( $1.6$   $\text{J}/\text{cm}^2$ ), XRD measurements show that the films are partially crystalline (Fig. 3c) and in a NASICON phase as shown by the comparison with the spectrum of the NASICON target (Fig. 3a).

Resistivity measurements were performed using impedance spectroscopy. Resistivity at room temperature is between  $3 \times 10^7$  and  $5 \times 10^7$   $\Omega$  cm, depending on the deposition conditions. From resistance measurements between 30 and  $400^\circ\text{C}$ , the activation



Fig. 2. Micrograph of a NASICON thin film deposited at  $1.5$   $\text{J}/\text{cm}^2$  on a Raipore membrane.

energy was between 0.33 and 0.5 eV, increasing with increasing resistivity. The measured resistivities are greater than the best reported values for bulk crystalline NASICON,  $1 \times 10^7$   $\Omega$  cm<sup>2</sup> and for bulk amorphous NASICON  $2 \times 10^8$   $\Omega$  cm<sup>2</sup>.

The performance of the membranes was evaluated by measuring the current efficiency for the production of sodium hydroxide from sodium sulfate using electrolysis. This is defined as the ratio of the actual quantity of base equivalent produced to the expected quantity calculated using Faraday's law, from the current density applied:  $\eta = I/F$  where  $I$  is the current density,  $t$  is the duration of the application of the current density,  $i$  is the number of equivalents expected, and  $F$  the Faraday constant ( $96,485$  C mol<sup>-1</sup>).

Figure 4 shows the cumulative current efficiencies of a composite membrane, and of a Raipore membrane. The composite membrane was made by depositing a 300 nm thick NASICON film at  $1.4$   $\text{J}/\text{cm}^2$  energy density on a fresh Raipore surface. The base cumulative current efficiency is the ratio of the number of moles of base produced over the total number of moles of electrons that crossed the cell since the beginning of the experiment. The cumulative current efficiency at high concentration is 58% for the Raipore membrane and 69% for the composite membrane. This 13% increase of the cumulative current efficiency represents a 23% improvement from the initial characteristics.

To help understand the origin of this improvement we measured the dc resistance of the Raipore and the composite membranes in two different solutions, in a 32%  $\text{H}_2\text{SO}_4$  solution, where conduction is essentially due to  $\text{H}^+$  ions passing through the membrane, and a 10%  $\text{NaOH}$  solution, where  $\text{Na}^+$  are the conducting ions. The

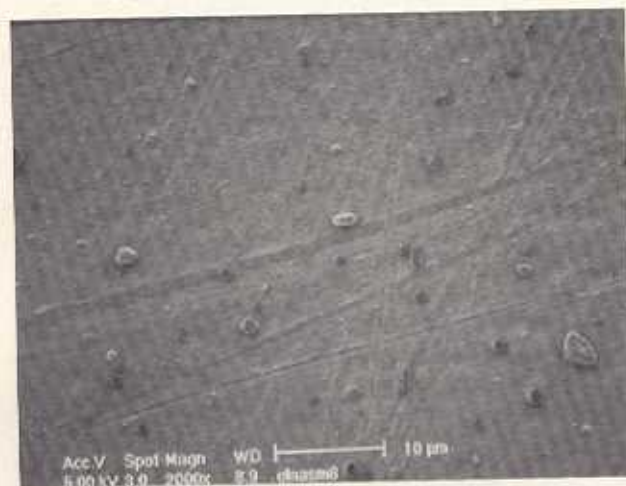


Fig. 1. Micrograph of a NASICON thin film deposited at  $0.72$   $\text{J}/\text{cm}^2$  on a Raipore membrane.

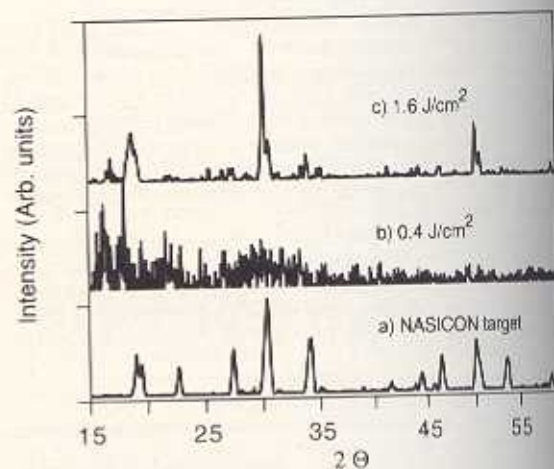


Fig. 3 XRD spectra of: (a) NASICON target, and thin films deposited at: (b) low energy density ( $0.4$   $\text{J}/\text{cm}^2$ ) and (c) high energy density ( $1.6$   $\text{J}/\text{cm}^2$ ).



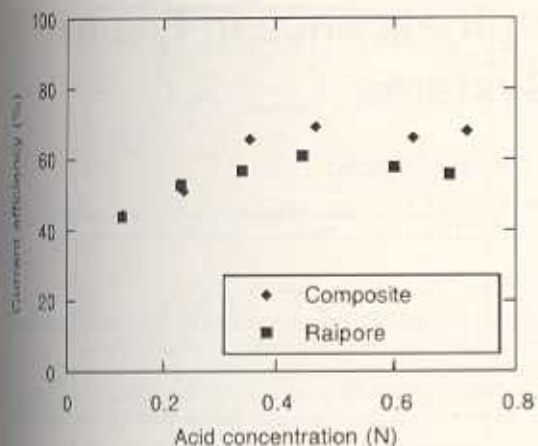


Fig. 4. Cumulative current efficiency of Raipore and composite membranes as a function of acid concentration. The composite membrane was made by depositing a 300 nm thick NASICON film at 1.4 J/cm<sup>2</sup> energy density on a fresh Raipore surface.

The resistance of the composite membrane is higher in both solutions. This is to be expected, since in the composite membrane the resistance of the NASICON is in series with the resistance of the Raipore. However, the increase of resistance for the H<sup>+</sup> ions, 6.7 Ω, is higher than for the Na<sup>+</sup> ions, 5.0 Ω. The increase of efficiency seems to be because the composite membrane is more selective toward H<sup>+</sup> ions than the Raipore membrane. Another indication of this is the transfer of water from the catholyte side to the anolyte side of the cell. As this transport is due to transport of H<sub>3</sub>O<sup>+</sup> ions, the water should be transferred by the composite membrane. In the same conditions, after 90 h of operation, 28 ml of water are transferred when using the Raipore membrane and only 23 when using the composite membrane. This indicates once more a better selectivity against H<sub>3</sub>O<sup>+</sup> transport for the composite membrane.

The durability of the membrane is another important criterion in the evaluation of the performance of the composite membrane. We have measured the dissolution of thin films of NASICON in acid solution. It has been reported to be a problem<sup>10,11</sup>, and the long-term operation of the composite membranes. The scratch test<sup>12</sup> was used to evaluate the adhesion of the NASICON film to the polymeric membrane. Quantitative analysis could not be performed because the polymer shows cohesive failure before delamination takes place. However, we may conclude that the adhesion is good. In the dissolution experiment, a thin film of NASICON deposited on Si<sub>3</sub>N<sub>4</sub>/Si was placed in a high concentration sulfuric acid solution. After 1 week, 40% of the thickness of NASICON was dissolved; after 2 weeks no further decrease was observed. Finally, the membrane was subjected to over 80 days of continuous operation in an electrolysis cell. No decrease of efficiency was observed. This confirms the durability of the composite membrane (longer tests are in progress).

The life of a membrane can also be influenced by its resistance to fouling agents such as iron, calcium, and magnesium. The foul-

ing process occurs through the precipitation of the hydroxide salts of these agents inside the membrane when these ions cross it and encounter a relatively high concentration of hydroxide on the catholyte side of the membrane. To compare the resistance of each membrane to fouling, measurements were performed in the same electrolysis cell, but the anolyte was charged with 275 ppm of ferrous sulfate. After only 4 days of operation, the Raipore membrane failed. In contrast, the composite membrane functioned for 26 days in the same conditions, and was still functioning when the experiment was terminated. More complete results on this and on membrane selectivity will be reported elsewhere.<sup>13</sup>

### Conclusion

NASICON thin films can be deposited by PLD. The deposited films are good ionic conductors. Composite ion selective membrane can be fabricated by depositing a thin film of NASICON by PLD on a Raipore membrane. This composite membrane has better efficiency and resistance to fouling than the Raipore membrane. Thus, this represents a promising technological development.<sup>14</sup>

### Acknowledgments

The authors acknowledge, for financial support, the Natural Science and Engineering Council of Canada (NSERC), Pulp and Paper Research Institute of Canada (PAPRICAN), and the Fonds pour la formation de Chercheurs et l'Aide à la Recherche (FCAR) of Quebec.

Manuscript submitted July 15, 1997; revised manuscript received Aug. 20, 1997.

École Polytechnique de Montréal assisted in meeting the publication costs of this article.

### REFERENCES

1. M. Paleologou, J.-N. Cloutier, P. Rananyergtm, R. M. Berry, M. K. Azaeniouch, and J. Dorica, *Pulp Pap.*, **95**, T386 (1994).
2. J. B. Goodenough, H. Y.-P. Hong, and J. A. Kafalas, *Mater. Res. Bull.*, **11**, 203 (1976).
3. A. V. Joshi, M. Liu, A. Bjorseth, and L. Renberg, U.S. Pat. 5,290,405 (1994).
4. Y. L. Huang, A. Caneiro, M. Attari, and P. Fabry, *Thin Solid Films*, **196**, 283 (1991).
5. A. Ahmad and T. A. Wheat, *Solid State Ionics*, **76**, 143 (1996).
6. D. B. Chrisey and A. Inam, *MRS Bull.*, **XVII**, 37 (Feb. 1992).
7. R. Izquierdo, F. Hanus, Th. Lang, D. Ivanov, M. Meunier, L. Laude, J. F. Currie, and A. Yelon, *Appl. Surf. Sci.*, **96-98** (1996).
8. M. C. Foote, R. P. Vasquez, B. B. Jones, B. D. Hunt, and J. B. Barner, *J. Electron. Mater.*, **23**, 849 (1994).
9. J. P. Boilot and Ph. Colomban, *Solid State Ionics*, **18&19**, 974 (1986).
10. D. Sutija, S. H. Balagopal, T. Landro, and J. H. Gordon, *Interface*, **5** (4), 26 (1996).
11. S. H. Balagopal, J. H. Gordon, A. V. Virkar, and A. V. Joshi, U.S. Pat. 5,580,430 (1996).
12. M. Ohring, *The Materials Science of Thin Films*, p. 445, Academic Press, San Diego (1992).
13. F. Girard, R. Izquierdo, E. Quenneville, M. Meunier, D. Ivanov, M. Paleologou, and A. Yelon, To be published.
14. A. Yelon, M. Paleologou, D. Ivanov, R. Izquierdo, and M. Meunier, U.S. Pat., Submitted.