

**Energy Efficient Process for Recycling Sodium Sulfate
Utilizing Ceramic Solid Electrolyte**

Final Report

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1.0

Abstract

A major development effort was undertaken at Ceramatec to increase the sodium transport rates and transport efficiency of NaSICON membranes for recycling sodium sulfate. A novel NaSICON composition (NAS-D) and its doped versions were developed that exhibit excellent resistance to corrosion in acid and alkaline electrolytes. The NAS-D based membranes show exceptionally high sodium transport efficiency (> 92 %) in caustic for over 5000 hours of operation. While the chemical stability in acid was excellent, there is a need to arrest the ion exchange of H⁺ or H₃O⁺ for Na⁺ ions at the monolayer of the NaSICON membranes in acidic anolyte (pH < 4) in order to make them viable for commercial electrochemical application such as recycling of sodium sulfate.

A series of new NaSICON compositions were synthesized (NAS-E, NAS-G and NAS-H). The sintering conditions of these new materials were optimized to develop single-phase ceramic membranes with density higher than 98% of theoretical, and zero surface porosity. These membranes have exhibited high conductivity at room temperature (5×10^{-3} S/cm at 22° C) in alkaline and acidic electrolytes. The sodium ionic conductivity of NAS-G is three times higher than that of the NAS-D composition. The NAS-G membrane exhibits a conductivity of 1.9×10^{-2} S/cm at 65°C, which is the highest conductivity measured in our laboratory or ever reported in technical literature. These membranes were operated in single membrane electrochemical cells in pure NaOH and complex salts between 25 and 400 mA/cm² current density at 40° C for over 5000 hours of operation. The sodium transport efficiency in alkaline solutions was greater than 92 %. The exceptionally high conductivity of these membranes allows them to transport higher current without a significant change in driving voltage across the membrane. A single membrane (NAS-G) electrochemical cell was operated at 600 mA/cm², the driving voltage was 2 volts at 65° C, across a 0.7 mm thick membrane.

The chemical stability of these new NaSICON materials is excellent in acidic as well as caustic solutions. A weight change of 0.1 % per 1000 hours of testing was observed over 150 days of testing. The ionic conductivity in acid electrolyte was hampered by the exchange of H^+ ions, for Na^+ ions at the monolayer sites in the membrane whose primary function is to exchange sodium ions at the electrolyte membrane interface.

2.0

Project Objective

The objective of the program was to develop a novel energy-efficient electrochemical process for recycling waste sodium sulfate and convert it to sodium hydroxide and sulfuric acid using solid ceramic electrolytes. Ceramatec's proprietary NaSICON materials have exhibited high selectivity towards sodium ions over hydronium and alkali ions, which gives the process an inherent advantage over competing technologies relying on polymer membranes.

Ceramatec undertook a set of tasks to develop, test and optimize the NaSICON materials. Ceramatec also performed electrochemical tests for screening purposes, and to characterize the performance of membranes as a function of process conditions (i.e. voltage, temperature, fluid flow rate, and corrosion resistance). The performance criteria was to achieve 1000 hours of operation at a minimum of 100 mA/cm² current density with sodium transport efficiency higher than 90 % in Na₂SO₄ feed. The tests focused on determining the optimal conditions for using these membranes, and also evaluated the membrane stability in nitrate/nitrite containing solutions.

3.0

Introduction

Sodium sesquisulfate $\text{Na}_2\text{S}_2\text{O}_8$ (also known as saltcake) or sodium sulfate (Na_2SO_4) are the by-products of chlorine dioxide generation process in the pulp and paper industry. The separation of alkali ions in solution has diverse applications in traditional industrial processing. NaSICON holds promise for electrochemical recycling of sodium sulfate saltcake produced in the pulp and paper industry, particularly in bleached pulp mills, to produce caustic and weak sulfuric acid, much of which can be used on-site at the mills. A process that recycles sodium sulfate saltcake will allow the paper and pulp industry to lower costs for chlorine dioxide generation. An economically viable process for recycling the sodium sulfate into usable products currently does not exist. The ceramic membrane based electrochemical process is expected to be economically viable because of its relative energy efficiency and the lack of fouling of the membranes during cell operation.

Although the majority of sodium sulfate is used as a make-up chemical for the kraft recovery cycle, there is a huge stock pile of Na_2SO_4 that can be recycled. Currently in the U.S., about 800,000 tons per year of sodium sulfate is either sewered or landfilled. Salt-splitting technology will prevent the sewerage of excess sodium sulfate and enable the production of about 550,000 tons per year of valuable caustic soda and about 675,000 tons per year of sulfuric acid to be used for chlorine dioxide production. The availability of quality ion-conducting membrane that possess high sodium ion conductivity ($>10^{-3}$ S/cm), high selectivity to sodium over hydronium and other ions ($> 90\%$), and excellent chemical stability in acidic and alkaline solutions ($< 0.1\%$ degradation per 1000 hours) is required to commercially use the ion-conducting membrane technology for recycling sodium sulfate as a low energy consumption process.

The electrochemical conversion of Na_2SO_4 is based on water electrolysis according to the electrode reactions (1.1) and (1.2), and the selective transport of Na^+ ions from anode to cathode compartment of the cell through the ionic-conductive membrane.



Thus the overall reaction for the electrochemical conversion of Na_2SO_4 is given by



Currently, the organic polymer membranes developed for industrial chlor-alkali electrolysis, such as perfluoro-sulfonic-acid-based Nafion™, have been tested for electrochemical conversion of Na_2SO_4 . These membrane, however, are not highly specific to sodium ions, they allow cations other than sodium to pass through them. In addition, ions such as Mg^{2+} , Ca^{2+} and Al^{3+} that are sparingly soluble at an intermediate pH precipitate in the polymeric membranes causing it to foul. The sodium super ionic conductors or NaSICON, developed at Ceramatec could be used as electrolysis membranes for Na_2SO_4 recycling. Ceramatec's proprietary NaSICON materials that were developed under phase I of the current DOE program, are highly conductive and selective to sodium ions over hydronium and other cations and anions. In addition, the precipitation of sparingly soluble hydroxides of 2^+ and 3^+ cations does not influence the performance of ceramic membranes. Based on the merits of ceramic membranes for waste recycling, the research at Ceramatec focused on validating the membrane properties at the pertinent operating conditions for salt splitting application.

4.0

Narrative Summary

Ceramatec began work on sodium-conducting membranes in 1976, which resulted in the development of highly conductive sodium beta alumina (β'' -Al₂O₃), for high temperature Na-S battery application. Other sodium conductors such as Na₃Zr₂Si₂PO₁₂ (NZP) and RE-NaSICON, Na₅RE₃Si₄O₁₂ were also explored as alternatives.

The feasibility study of NaSICON membranes in electrolysis of aqueous solution of sodium sulfate was initiated in 1990. Since then we have demonstrated that the NaSICON membranes can be used to produce high concentration of caustic and acid at high current efficiency (> 80 %) from waste Na₂SO₄ salt cake. While the selective transport of sodium ions through the NaSICON membrane is excellent, the ionic conductivity was considered low for practical commercial applications. Therefore, a new series of NaSICON materials were developed with emphasis on ionic conductivity. During 1991, Ceramatec started an extensive material development program to develop highly conductive and chemically stable compositions for salt spitting application. The new compositions were developed to increase the physical and chemical stability in acidic electrolytes. This program showed that slight modification in composition can improve the corrosion resistance of the membranes in acidic electrolyte, but the ionic conductivity was not high enough to economically recycle Na₂SO₄ salt cake.

A follow-up program was undertaken with the RE-NaSICON family of materials that yielded Dy and Nd-NaSICON compositions. The sodium ionic conductivity of these materials at 70° C was 1x10⁻³ S/cm. The Dy and Nd NaSICON membranes have performed at sodium transport efficiency of above 95% in sodium bearing acidic and caustic electrolyte, at current density up to 250 mA/cm². Despite the high stability

exhibited by these membranes in concentrated caustic electrolyte their corrosion resistance in concentrated sulfuric acid was poor. Further development was required to increase the membrane operational lifetime in concentrated sulfuric acid.

An acid-resistant NaSICON composition was successfully developed during phase I of the project in 1991. This composition was applied as porous coating (10 μm thick) on the Dy-NaSICON membrane. The composite membrane was tested in a pH 0.2 anolyte solution containing 1M Na_2SO_4 , and an alkaline catholyte solution (1M NaOH). Although the current efficiency was modest (~40%), the coated layer protected the Dy-NaSICON membrane from degradation during the first 1000 hours of operation at 90 mA/cm^2 current density. However, the membrane was chemically attacked after 1000 hours of operation, when the conductivity fell rapidly. Thus, further development of material composition and/or coating was identified as a developmental issue.

During 1996, various sodium bearing glass coating materials that are known to have excellent corrosion resistance properties were developed as coating materials. Although the glass compositions exhibited poor ionic conductivity, they were extremely resistive to corrosion. We were unable to deposit dense glass coating on membranes due to sintering limitations. Two proprietary compositions which had low sodium ionic conductivity were found to have good chemical stability in acidic sodium sulfate solution for over 4000 hours when tested at 60° C. However, the deposited coating was porous, and the base membrane was still attacked after few thousand hours of operation. These coatings provided a physical barrier for over 1000 hours of operation, and ultimately the membrane weakened. Due to the difficulty in achieving dense and thin corrosion resistant coatings both from fabrication as well as functional perspective, our effort was directed towards modifying the base membrane composition.

By the end of 1996, a novel base-tolerant, NAS-D composition was discovered which exhibit high sodium transport efficiency in caustic (> 92% for over 5000 hours) without any break-in period as observed with the Dy-NaSICON. In addition, a new coating material (NAS-A) with similar thermal properties as NAS-D was developed. The

NAS-A material showed excellent corrosion resistance in acidic electrolyte (1M H₂SO₄ + 1M Na₂SO₄) for over 3500 hours at 60° C. The NAS-A composition was successfully deposited on NAS-D and co-fired with the membrane into a dense coating.

A series of doped NAS-D compositions were synthesized and screened to evaluate the electrochemical performance in Na₂SO₄ based complex salt simulants. It was previously demonstrated that the corrosion resistance of the doped RE-NaSICON compositions improved in acidic solutions with doping, although the conductivity was low. The doped NAS-D membranes showed excellent chemical stability in acidic (pH 0.6) as well as alkaline (pH 14) solutions. The NAS-D and its doped versions were operated in single membrane electrochemical cells. The sodium current efficiency was greater than 90 % during electrolysis in alkaline electrolyte in tests that exceeded 3000 hours at modest current densities ranging from 25 to 50 mA/cm². However, in acidic electrolyte, the conductivity of NAS-D based membranes showed initial promise but eventually the cell performance dropped after 250 hours of operation.

A major breakthrough in NaSICON technology was achieved during the middle of 1997 when a series of new NaSICON compositions were synthesized (NAS-E, NAS-G, and NAS-H). The conductivity of NAS-G membrane was more than three times that of NAS-D composition. The conductivity of NAS-G membrane at 65° C was 1.9x10⁻² S/cm; this is the highest sodium ionic conductivity ever measured at our facility.

The NAS-G, NAS-E and NAS-H membranes performed at greater than 92 % sodium transport efficiency during electrolysis of complex salts. A single membrane cell was operated at current density as high as 400 mA/cm². Furthermore, due to the exceptionally high ionic conductivity of the new membrane series, it is feasible to operate at high current without a significant increase in driving voltage. A single membrane NAS-G cell was operated at 600 mA/cm² and 65°C, with a driving voltage of 2 volts across a 0.7 mm thick membrane. The chemical stability of these new ceramic materials is excellent in acidic and caustic electrolytes. Unfortunately their electrical conductivity in acid electrolytes was hindered by the ion exchange of H₃O⁺ ions.

5.0

Development of Second Generation Membranes

The objective of the present DOE program under phase 1, was to develop and characterize the new membrane compositions for salt splitting application with improved electrochemical life time, ionic conductivity and transport efficiency. The objective for testing the new membrane series was to validate these improvements.

The material development strategy was two-fold. The first part of the strategy was to alter the conducting channel size of the NaSICON structure to increase the sodium ion conductivity. The second part of the strategy was to improve the membrane durability. These strategies resulted in the discovery of new material series (NAS-D, NAS-E, and NAS-G). We optimized the sintering conditions of these new materials, and developed membranes with density higher than 98% of theoretical with zero surface porosity (Figures 1, and 2).

5.1 Fabrication of NaSICON membranes

During the phase 1 of the program, the new NaSICON compositions were synthesized using the standard process of mixing the precursor followed by calcination. The calcined powder was milled to achieve the pre-requisite surface area. circular disks (1.25 inches in diameter) were pressed with a die assembly and were fired in air over a wide temperature range to sinter the membranes. The calcination and sintering schedules were developed to maximize the membrane density. This material was made free of impurity phases. The presence of impurity phases has historically resulted in poor conductivity of NaSICON membranes for applications below 100° C.

The doped NAS-D compositions were processed with the aim to improve the corrosion resistance and ionic conductivity of the membranes in acidic electrolyte (pH<2). We have previously demonstrated with the Dy-NaSICON membranes that the corrosion resistance in acidic solutions improves significantly with dopant. The doped NAS-D compositions were synthesized and sintered to full density (Figures 3, and 4).

The NAS-A, a corrosion resistant composition, was applied on the NAS-D membrane by dip coating. The sintering characteristics and the thermal properties of these two materials were similar which enabled the co-firing of the membranes to form a dense composite. The interface however showed areas of delamination across the cross section of the membrane.

5.2 Characterization of NaSICON membranes

It is historically evident with the NaSICON related materials that presence of resistive secondary phases lowers the ionic conductivity at temperatures below 100° C. X-ray diffraction and microstructure analysis (SEM) was performed on the compositions to verify the phase purity and morphology of the membranes.

The new base-tolerant NAS-D material that was synthesized in October of 1996 was found to be pure single-phase based on x-ray diffraction analysis, and no evidence of secondary phase was evident from the microstructural analysis (Figure 5). The doped NAS-D compositions have retained the crystal structure of NAS-D, and solid solution phases were formed in the range of dopant concentration. We confirmed by x-ray analysis that the NAS-E, NAS-G, and NAS-H form solid solution compounds in the dopant concentration range studied. This indicates that the sodium conducting phases are retained in these compositions. There was no evidence of secondary phases in the doped compositions that can lower the sodium ionic conductivity of the membranes at temperatures between 40 and 60° C.

5.3 Chemical stability of NaSICON membranes

The chemical durability of NaSICON series was analyzed in the absence of electric field in acidic and alkaline solutions. The NaSICON membranes were immersed in aqueous electrolyte solution and tested at constant temperature of 40° C. The membranes were periodically taken out of solution, washed in water and the weight was measured. The tests were carried out over several thousand of hours. This test measures the rate of corrosion of the membranes in electrolyte solution.

The NAS-D membrane was tested in 1.5M NaOH solution at 40° C. The membrane was chemically stable in tests that lasted over 150 days. The chemical durability (corrosion resistance) of NAS-D membranes was also tested in the presence of an electric field in a two-compartment electrochemical cell in acidic anolyte (pH 0.2), and caustic catholyte (pH 14) at 40° C. The membranes were caustic-tolerant owing to high stability against corrosion in caustic solution, but when the membranes were tested in acidic anolyte, they were attacked by the acid after 2000 hours of operation. This prompted the development of a protective coating on the anode side of the NAS-D membrane for use in recycling sodium sulfate.

A new anolyte coating material NAS-A was synthesized which is a doped version of NAS-D. A monolith NAS-A sample showed superior resistance to corrosion when tested in acidic solution (1M H₂SO₄ + 1M Na₂SO₄, pH=0.2) at 60° C. The membrane showed less than 1 % weight loss after testing for 3500 hours (Figure 6). A thin coating of NAS-A (3 micron) was deposited on the NAS-D membrane and co-fired. The fractured cross section of the fired composite was evaluated under the scanning electron microscope (Figure 7). The coating thickness estimated to be around 25 microns, was weakly bonded across most part of the interface with the NAS-D membrane. The current density (2.5 mA/cm²) was lower when the coated membrane was tested in acidic electrolyte which we attribute to delamination at the interface.

The doped NAS-D compositions were tested in acidic solutions. The stability of the membranes tested in acidic solution containing 1M H₂SO₄ + 1M Na₂SO₄ is shown in Figure 8. Similar to Dy-NaSICON, the doped NAS-D membranes show excellent resistance to corrosion in low and high pH solutions. The ionic conductivity of the NAS-D based membranes is excellent in alkaline solutions, but it is poor in acidic solutions, again owing to protonic ion-exchange with the membrane.

The two membranes compositions NAS-E and NAS-G with the best ionic conductivity, were subjected to static corrosion testing in 1.5M NaOH solution at 40° C. The membranes show less than 0.1 % weight loss in 150 days of continuous testing (Figure 9).

In conclusion, the new generation of NaSICON membranes (NAS-D, NAS-E and NAS-G) have excellent chemical stability in both acidic and alkaline solutions in the absence of electric field. This is a significant improvement in membrane lifetime compared to RE-NaSICON membranes that were previously developed for recycling Na₂SO₄.

5.4 Electrical conductivity of NaSICON membranes

The ionic conductivity of NaSICON materials was measured in the temperatures ranging from 22° C to 65° C in a custom designed electrochemical cell (Figure 10). It is a two-compartment cell with the NaSICON membrane sealed with O-rings between two parallel plates in the center of the cell body. The cell uses four electrodes, platinum or nickel anode, a nickel cathode, and two reference electrodes (saturated calomel electrodes, SCE) that are inserted in custom-designed Luggin capillaries whose tips touch the membrane on either side. The ionic conductivity of the membranes was based on measuring the potential difference between the two reference electrodes (equivalent to driving voltage across the membrane) created by a known amount of current passing through the cell. Since the membrane is hermetically sealed, the total cell current is assumed to pass through the membrane. The conductivity of the individual membrane is

calculated with equations.

$$\Delta U = RI \quad (1.4)$$

$$R = \ell / \sigma S \quad (1.5)$$

Where, ΔU is the potential difference between the two reference electrodes, I the current passing through the membrane, R the membrane resistance, ℓ the membrane thickness, S the projected surface area of the membrane (surface of one side of the membrane) and σ the electrical conductivity of the membrane.

Several techniques such as A.C. impedance, linear sweep voltammetry (LSV), current interrupt, and steady-state were used to validate the ionic conductivity of the membranes. The A.C. impedance and current interrupt techniques were used in open circuit conditions (in the absence of current), and the linear sweep voltammetry, steady-state, and the current interrupt techniques were used under the influence of electric field, *i.e.* at varied current densities through the membrane.

The sodium ionic conductivity of the new NaSICON series measured in caustic solutions by the LSV technique is shown in Figure 11. The conductivity of NAS-G membrane increases as a function of temperature as expected, but it also increases as a function of current density. Similar dependency in ionic conductivity on current density was observed with the current interrupt technique, where the current pulses are superimposed at different constant current. The conductivity is higher when the constant current is larger. This non-ohmic behavior is typical for charge transfer related kinetics across an electrochemical double layer such as at the electrode-electrolyte interface. Due to the electrochemical double layer conditions existing at the membrane-electrolyte interface, the non-ohmic behavior in ionic conductivity of the membrane can be attributed to the presence of interfacial charge transfer resistance.

In general, the A.C. impedance technique is most useful to separate out various components of the overall cell resistance of an electrochemical system while determining the bulk resistance of the membrane. The resolution of the individual components in an A.C. impedance spectrum is determined by the ratio of capacitance to resistance. The capacitance, and the interfacial resistance of the NaSICON-electrolyte interface is very small when compared to the bulk resistance of the membrane. The measurements at higher frequencies (above 10 kHz) to separate out the bulk and grain boundary resistance from the electrode and interfacial resistance was disturbed by the inductive components of the leads. Therefore, we were obliged to report the total resistance of the membrane.

It is evident from the measurements made as a function of Na^+ concentration in the electrolyte (Figure 12), that the interfacial resistance at the membrane-electrolyte interface is very low. We observed that the ionic conductivity of the membranes increases inversely to sodium ion concentration (NaOH or NaCl solution) in static electrolyte conditions, this we attribute to low sodium charge transfer resistance at the interface. However, the sodium ion concentration below 0.1M is not suitable for continuous operation of NaSICON membranes at current densities higher than 100 mA/cm^2 due to concentration polarization in the solution. The ionic conductivity of NaSICON membranes is independent of the solution pH (above 7), and the performance of the membrane is not influenced by the presence of Cl^- ions (Figure 11).

The non-ohmic behavior in ionic conductivity of NaSICON membranes can be explained by the conducting mechanism theory of ions through the oxide solid phase described by Cabrera-Mott¹. According to this theory the ionic current density in the oxide in the high-field approximation is given by

$$j = 2a\sigma v n \exp\{-(E_a - qa\xi)/kT\} \quad (1.6)$$

where, a is the half-jump distance for the ions ($2a$ = distance between interstitial sites), v the vibration frequency of ions, n the concentration of ions, E_a the activation energy for motion between interstitial sites, q the charge on the mobile ion, ξ the electric field, k the

Boltzman constant, and T the absolute temperature. The equation (1.6) describes the non-ohmic behavior.

The ionic conductivity of new NaSICON membranes measured by LSV technique in caustic electrolyte is shown in Figure 12. The conductivity of NAS-E, NAS-G and NAS-H is higher than that reported for Dy-NaSICON². The conductivity of NAS-G is an order of magnitude higher than that of Dy-NaSICON. These results were also confirmed by A.C. technique. The energy of activation for sodium ion conduction through NaSICON membranes was calculated to be 27.0 kJ/mol.

The membrane-electrolyte interface resistance in caustic solution is very small in comparison to the bulk resistance of the membrane as evident from the A.C. impedance spectra. This conclusion was based on the conductivity measurements performed with membranes at different thickness. However, in acidic solutions, the interfacial resistance reaches 100 times higher than that in caustic in a matter of hours. This is likely caused by H_3O^+ ions that exchange with Na^+ ions at the monolayer of the membrane. Due to the ion exchange induced mechanism, the Na^+ ion sites at the membrane monolayer decreases considerably under the influence of electric field during testing in sodium sulfate anolyte, which significantly increases the interfacial resistance (IR) for Na^+ ion exchange at the interface.

When the IR drop increased in impedance analysis after testing the NAS-E membrane in acidic electrolytes for 25 hours. We can conclude that the Na^+ ion transport through NaSICON membranes in acidic solution is limited by the membrane-electrolyte interface resistance rather than the bulk properties of the membrane.

6.0

Electrochemical Testing Setup

The new series of NaSICON membranes were electrochemically tested in single membrane cells in acidic and caustic aqueous electrolytes. The operational lifetime, sodium efficiency, and the conductivity of membranes were evaluated during the cell operation. A single membrane cell configuration with or without electrolyte flow through design was used. The membrane (1.0 inch in diameter, and 0.7 mm or standard, 1.4 mm in thickness) is hermetically sealed with O-rings between two holders in the center of the cell. Prior to assembly, the quality of the membrane was checked with a helium leak detector. In addition, the cell was subjected to pressure test after assembly to check for leak before tests were carried out.

The cells were operated either at constant voltage (typically 4.5 V) or constant current (100-400 mA/cm²) based on the membrane composition at temperatures between 40 and 60°C. The electrolyte feed was maintained at 1.5 gallons per minute when testing the single membrane cells. The cells were operated in a batch mode by periodically replacing the aqueous sodium based electrolyte with a new batch. Nickel anode was used in alkaline tests, and in acidic and chloride containing electrolyte, platinum anode was used.

Two types of cell were used for electrochemical testing, the vertical and horizontal flow through design for continuous testing, and the static cell design for characterization of membranes. The sodium transport efficiency was determined periodically by titration of the anolyte and catholyte with HCl or NaOH solutions depending on the nature of the electrolyte. The sodium transport efficiency was measured by this technique only when Na⁺ and H₃O⁺ cations are present in the

electrolyte. While testing with complex electrolyte that contain multitude of cations, the titration technique was used for qualitative analysis purpose only.

6.1 Static cell setup

The static cell is divided by a membrane holder that houses a ceramic membrane disc sealed between two O-rings. The cell body seals against the membrane holder with gaskets to form an open-top cube that holds approximately 400 ml of the electrolyte solution in the anolyte and catholyte compartments. Long quarter inch bolts run through the cell and the membrane scaffold that holds the cell together, and provides sealing. It has a removable top cover that holds the working electrodes in place (Figure 10). Two L-shaped glass tubes (Luggin capillary) can be inserted in the anolyte and catholyte that touches the membrane surface. The reference electrodes are placed in the L-shaped tubes. The glass tube filled with the electrolyte allows the reference electrodes to measure the potential drop across the membrane by avoiding the potential at the electrodes and the solution. The cell is placed in a temperature-controlled water bath to maintain the aqueous electrolyte at a desired temperature. The simple design of the static cell was modified to a flow through cell with inlet and outlet flow ports for high current testing.

The static cell design was used to measure the driving voltage across the membrane to monitor the performance of membrane independent of the cell operation. The voltage across the membrane was measured with two saturated calomel reference electrodes placed in custom-designed Luggin capillaries which touches the membrane on either side.

A current or voltage source, i.e. either a potentiostat or an ac impedance / gain-phase analyzer, is connected to the working and counter electrodes to provide the electrochemical driving force for the reaction. A measuring device such as an oscilloscope, x-y-recorder, was attached to the reference electrodes to measure the voltage across the membrane being tested. The A.C. impedance measurement set up

consists a Shlumberger S1286 Electrochemical Interface and a Shlumberger S1260 Impedance/Gain-Phase analyzer linked to the electrochemical cell. A EG&G Princeton Applied Research Potentiostat/Galvanostat was used to generate the DC-pulse currents in for current-interrupt tests.

6.2 Flow-through cell setup

The long-term cell consists of two sets of two identical HDPE plates, that have pockets cut into them to allow fluid to flow through the cell. The inner set of plates contains a fluid channel, with an O-ring groove to seal a ceramic membrane in place. The outer set of plates contains inlet and outlet ports to allow electrolyte solution to continually recirculate through the cell. The plates are sealed together with rubber gaskets. Quarter-inch bolts run through the cell to hold the cell together and provide sealing. A titanium post, sealed with O-rings, runs through the outer plates, and screws into electrodes positioned near the surface of the membrane.

A peristaltic pump draws electrolyte solution from holding tanks, and pumps the fluid to the inlet of the assembled cell. The electrolyte solution returns to the holding tanks from the outlet of the cell by gravity-feed. The holding tanks sit atop a temperature controlled hot-plate which heats the solution to the desired electrolyte temperature.

The cell is connected to a DC power supply and a computerized data acquisition system that records the cell voltage, current, and temperature at specified time intervals.

7.0

Electrochemical testing and performance evaluation

The electrochemical test results of NaSICON membranes in single cell scaffolds are presented. The tests were conducted with membranes at 0.7 mm and 1.4 mm thickness in horizontal and vertical cell configurations, at current densities between 25 and 600 mA/cm².

7.1 Testing approach and Strategy

The approach during the Phase 2 of the program, was to evaluate the performance of the new membranes as a function of current density and membrane lifetime. The electrochemical performance of the membrane series (NAS-D, NAS-E, NAS-G) were evaluated in alkaline and acidic electrolytes.

The new series of NaSICON materials were synthesized and developed during 1997. The program goal was to develop new NaSICON compositions, and test them at current densities higher than 100 mA/cm² in Na₂SO₄ and NaOH electrolytes. During first phase of the program (1997), the sodium ionic conductivity of NAS-D, NAS-E and NAS-G based membranes were measured in NaOH and Na₂SO₄ by A.C. impedance and LSV techniques. The most promising membrane compositions were down selected after the conductivity measurements for electrochemical evaluation.

7.2 Testing of NAS-D membranes in alkaline electrolyte

The doped NAS-D produced a proprietary material NAS-D10 that was able to operate for over 4000 hours at greater than 90% efficiency in a high-pH anolyte (Figure 13). This

cell was operated at a current density of 30 mA/cm^2 at 4.5 volts and 40° C . A current density of 200 mA/cm^2 was attained in a separate test with a 0.7 mm thick NAS-D10 membrane at higher cell voltage. The NAS-D50 membrane operated at higher conductivity than the NAS-D10 (Figures 14), and the initial sodium-transport efficiency was between 90 and 100%. Unlike the NAS-D10, the NAS-D50 membrane started to transport H^+ species in addition to Na^+ after several hundred hours of performance, which increases the total current. The fact that the total sodium current did not drop in these tests is indicative of structural changes in membranes (phase segregation) that could promote H^+ transport. X-ray analysis of the as sintered NAS-D25 and NAS-D50 membranes showed traces of secondary phase. The attack on the dopant dominant phase could promote protonic transport. It is evident from these electrochemical tests that the sodium transport efficiency remains high and steady at 90%, and most importantly, the NAS-D membrane is structurally stable during the length of the test.

The NAS-D and doped membranes were tested in a static cell design to evaluate the degradation phenomenon. The cell was operated at constant current density of 100 mA/cm^2 in caustic solution at 40° C (Figure 15). The purpose of these tests was also to establish a correlation between the doping concentration and membrane stability. The A.C. impedance measurements performed every 100 hours of testing in caustic electrolyte showed a gradual decrease in membrane resistance as the test continued. There was no major difference in the impedance spectra of the tested membrane in comparison to virgin spectra, except the membrane resistance was lower in the tested membrane. The possible explanation is that the membrane degrades due to a thinning mechanism when operated in static electrochemical conditions at a current density of 100 mA/cm^2 . The ionic transport at the stage when the membrane starts to show degradation is most likely by diffusion through the porous body. Hence, the driving voltage across the membrane remains constant after ~ 250 hours of operation. This test also concludes that the NAS-D membrane degrades if the operating current density is increased above 50 mA/cm^2 .

The beneficial effect of doping the NAS-D material was observed not only in the absence of electric field (or current), but also during electrochemical testing (Figure 16). The thinning rate of NAS-D10 membrane was lower than that of the undoped NAS-D which allowed the membrane to operate for longer period (~1000 hours). It is our conclusion that the undoped NAS-D membrane cannot operate at current densities higher than 50 mA/cm², whereas the NAS-D10 membrane can operate at current densities higher than 100 mA/cm².

7.3 Testing of NAS-G membranes in caustic electrolyte

Several NAS-G membranes were tested in NaOH electrolyte to study the effect of current density and sodium concentration on the membrane lifetime. The recycling of waste sodium sulfate saltcake using the ceramic membrane technology is based on electrochemical separation of alkali ions to produce caustic NaOH and weak sulfuric acid. It was important to establish the performance characteristics of the NaSICON membranes in caustic NaOH along side with the evaluation of the performance in sodium sulfate. Our aim was to separate out species other than sodium ions from the anolyte and estimate the true lifetime of the membrane in clean waste under electrochemical conditions. These tests were operated in static horizontal cells.

A NAS-G membrane was tested at 100 mA/cm² current density in constant current mode (Figure 17). The voltage across the membrane during the first 1100 hours of operation in 1.5 molar NaOH anolyte was 1 volt. We observed a fluctuation in voltage across the membrane during this testing period that was attributed to a lack of mixing of the electrolyte. The conductivity of the membrane remained stable during this testing period as measured by steady state and A.C. impedance techniques. The electrolyte was replaced with 5 molar NaOH after 1100 hours of testing, and the voltage across the membrane dropped to 0.6 volts at the same current density. Our hypothesis is the resistance of the membrane-electrolyte interface that dominates the mass transfer reactions decreases as a function of sodium ion concentration in the electrolyte. As a result, the conductivity of the membrane increases at higher sodium concentration.

A second NAS-G membrane was tested in a single membrane static cell in 5M NaOH electrolyte at 40° C. The membrane was operated in constant current mode at 200 mA/cm² current. The conductivity and voltage across the membrane remained stable during the first 1500 hours of testing. The average voltage across the membrane during this period of testing was 3.2 volts (Figure 18). There was a sudden drop in the driving voltage across the membrane as the test approached 1500 hours mark, and the voltage gradually approached the 1 volt before the membrane failed. We believe the thinning mechanism caused by erosion of the membrane explains for the gradual decrease in voltage, and an increase in ionic conductivity. Due to poor mixing of the solution in static cell, and aided by slow dissipation of gases that is generated during electrolysis of H₂O can cause the diffusion barrier for sodium ion exchange at the membrane electrolyte interface. The static test results clearly shows that the membrane degradation increases as a function of current density.

The performance of NAS-G membranes was evaluated as a function of operating current density and sodium concentration in single membrane electrochemical cells. A standard NAS-G membrane was tested in NaOH at a current density of 200 mA/cm² (Figure 19). This cell was operated for 1500 hours in a continuous batch mode at an average sodium transport efficiency of 92%. The average driving voltage across the membrane was about 3 volts. In a separate test, a NAS-G membrane was operated in a flow through cell in 5M NaOH at a current density of 400 mA/cm². The driving voltage across the membrane at this current density was 3.9 volts at 40° C. This cell performed at a sodium transport efficiency of 95 %.

In contrast to the NAS-D material, the doped NAS-G membrane does not show any improvement in membrane stability. A NAS-G10 membrane was operated in a static cell in 5M NaOH at current density of 200 mA/cm² (Figure 20). The thinning rate of the NAS-G10 membrane at 40° C was very high (3.8 mV/hour) in contrast to the NAS-G membrane, that decreased at 0.5 mV/hour after 1500 hours of testing under similar testing conditions.

A NAS-E membrane was tested in alkaline solution in a flow through electrochemical cell. The performance of this membrane was similar to the NAS-G membrane under similar testing conditions. The sodium transport efficiency of the NAS-E membrane was greater than 95% for over 750 hours of operation at 40° C. This cell was operated in 1.5 M NaOH at a current density of 100 mA/cm².

One can conclude from tests in caustic electrolyte that the electrochemical degradation of NaSICON membranes occurs dominantly under the influence of electric field (current). This complex process depends on several factors such as, electrolyte and membrane composition, current density (electric field), and the testing conditions. The scope of this project did not allow us to perform a systematic investigation of all the factors that influence the performance of NaSICON membranes in caustic and acidic electrolytes. However, the tests carried out so far have indicated that the operation lifetime of NAS-G membranes in alkaline electrolytes is longer than that of NAS-D membranes at current density higher than 100 mA/cm². The stability of the membranes decreases with an increase in operating current density (200 mA/cm²). The concentration of NaOH does not have any significant effect on the operation lifetime of the membranes, but the nitrate ions have an influence on membrane lifetime.

7.4 Electrochemical testing in neutral and acidic anolytes

In contrast to tests in alkaline solutions, the electrochemical performance of NaSICON membranes in neutral and acidic anolyte was not as promising due to interference of H₃O⁺ ions in the electrolyte that limits the ion exchange capacity of the membrane monolayer. The initial conductivity of NaSICON membranes in neutral and low pH solutions is similar to that in caustic electrolyte, but it significantly reduces as the interfacial resistance from the ion exchange process involving H₃O⁺ in solution and Na⁺ sites at the membrane monolayer increases. The interfacial resistance increases as the number of active Na⁺ sites at the membrane monolayer reduces.

The single membrane NAS-D was tested in a vertical flow through cell in 1 M Na_2SO_4 anolyte and 1 M NaOH catholyte. The sodium transport efficiency after 25 hours of testing in Na_2SO_4 (pH 2) anolyte was greater than 82% and the initial current density was 10 mA/cm^2 at a driving voltage of 4.5 volts. However, the interfacial sodium ion transfer resistance increased during this time due to the ion-exchange process at the anolyte-membrane interface, and the current dropped after 30 hours of testing to less than 2 mA/cm^2 .

The doped NAS-D membranes were tested in vertical electrochemical cells in 1M $\text{Na}_3\text{H}(\text{SO}_4)_2$ anolyte and 1.5M NaOH catholyte at 40°C . The transport efficiency of the cells operated with the doped membranes initially was between 82 to 100 % (Figures. 21-23). Similar to the NAS-D membrane, the current density was low in this test. The average current density during the first 150 hours of testing was between 1 and 2 mA/cm^2 at a driving voltage of 4.5 volts. The current density sharply increased after 150 hours of operation where the membrane failed. The failure of the membrane was likely caused by ion-exchange induced mechanism in acidic solution at high electric field. The dopant has improved the corrosion resistance of the NAS-D membranes in sodium sesquisulfate anolyte (pH < 2), but the sodium ionic conductivity of the membranes was still hampered by the H_3O^+ exchange.

A single membrane NAS-D was tested in acidic anolyte containing NO_3^- ions instead of SO_4^{2-} ions at 40°C . The electrochemical results were similar to that obtained in sulfate containing anolyte (Figure 24). During first 200 hours of operation the current was less than 10 mA/cm^2 at a cell driving voltage of 4.5 volts. After 200 hours of testing, the total cell current increased to 70 mA/cm^2 and the sodium current efficiency was 30%. However, in contrast to performance in sulfate containing acidic solutions, the NAS-D membrane in nitrate acidic anolyte operated for over 2500 hours.

The possible causes for low conductivity of NaSICON membranes in acidic solution was investigated by looking into the influence of various anions (OH^- , NO_3^- , and SO_4^{2-}). A single membrane static cell was used for these tests. Our hypothesis was

tested by generating the current-voltage polarization curves in NaOH solution with and without the presence of nitrate and sulfate ions (Figure 25). The current did not change significantly in the presence of nitrate or sulfate ions, which confirms that the anions don't interfere with the performance of NaSICON membranes in acidic solutions. Hence, the low current observed in NaSICON membrane cells when operated in sodium sesquisulfate anolyte (below pH 2) can be attributed to H_3O^+ ion exchange. One can explain that the membrane is initially dense and highly selective to Na^+ ion transport, as it gets porous under the aggressive attack of H_3O^+ ions and electric field, the membrane loses the ability to selectively transport sodium ions.

The performance of NAS-G membranes in neutral and acidic anolytes is similar to those obtained with the NAS-D membranes. A single membrane NAS-G was operated in neutral Na_2SO_4 anolyte (pH~9) at 22° C. The cell current was 50 mA/cm² at a driving voltage of 9.5 volts. However, as the pH of the anolyte become acidic the current drops to below 10 mA/cm² (Figure 26). The performance was similar when tested at 40° C. Polarization curves were generated with a single membrane NAS-G cell as a function of temperature in Na_2SO_4 anolyte (1M Na_2SO_4 + 0.2 M H_2SO_4) and 1.5M NaOH catholyte (Figure 27). The aim was to evaluate the influence of temperature on conduction mechanism in acidic electrolyte. In the three cases examined, the driving voltage across the membrane was high (~50 V at 40 mA/cm²) which indicates that the high resistance of the membrane (~360 Ω) is caused by the low pH of anolyte.

8.0

Conclusions/ Technological Assessment

Major development effort was undertaken to increase the sodium transport rates and transport efficiency of NaSICON membranes for recycling sodium sulfate. A novel NaSICON composition (NAS-D) was developed that shows excellent resistance to corrosion in acidic and alkaline electrolytes. The NAS-D based membranes were operated at sodium transport efficiency of higher than 92 % in caustic for over 5000 hours, at current density between 25 and 50 mA/cm². While the chemical stability of the NAS-D membrane was excellent in sodium sulfate, the ionic conductivity was limited by the interference of H₃O⁺ ions.

A series of new NaSICON compositions were synthesized (NAS-E, NAS-G and NAS-H) which have exceptionally high sodium ion conductivity at room temperature (5x10⁻³ S/cm at 22° C). The conductivity of NAS-G membrane is three times higher than the NAS-D. The NAS-G membrane exhibits a conductivity of 1.9x10⁻² S/cm at 65°C, this is the highest sodium ion conductivity measured in our facility.

The new NaSICON membranes are single-phase materials, the sintered density is higher than 98 % of theoretical, and show zero surface porosity. The membrane series were evaluated in single membrane electrochemical cells in acidic and caustic electrolytes. The performance of the membranes were investigated at different testing conditions to evaluate the influence of factors such as electrolyte composition, test temperatures, current density, and transport efficiency, on performance and lifetime of membranes for recycling sodium sulfate saltcake.

A single membrane NAS-G cell was operated at 400 mA/cm² in alkaline electrolyte with sodium transport efficiency of higher than 92 %. The exceptionally high ionic conductivity of the new membrane series allows them to be operated at high current density and moderate driving voltages. A single NAS-G membrane was operated at constant current density of 600 mA/cm². The driving voltage was 2 volts at 65° C across a 0.7 mm thick membrane.

The chemical stability of the new membrane series is excellent in acidic as well as caustic solutions (< 0.1 % degradation). Unfortunately their electrical conductivity in acidic electrolytes is considerably hampered by the H⁺ ions that exchange for sodium ions at the membrane monolayer when the anolyte condition drops below pH of 2, under the influence of electric field.

An efficient process to recycle sodium sulfate and actual saltcake effluent from a paper mill has been demonstrated on a laboratory scale. A Dy-NaSICON single membrane electrochemical cell performed at stable conditions for over 1000 hours, in batch mode operation with a pH 0.2 anolyte solution containing 1 M sodium sulfate.

A novel coating technology was developed under this program. The weight loss of the coating was less than 1 % after 3500 hours of testing at 60° C in 1M Na₂SO₄/1M H₂SO₄ electrolyte (pH = 0.2).

The lower ionic conductivity due to the protonic exchange in acidic anolyte at the membrane monolayer is still an unsolved issue. The protonic exchange for sodium ions in the membranes can be arrested with structural and compositional modifications.

Based on the results obtained to date from electrochemical testing in sodium based electrolytes, it is economically feasible to scale up and test a prototype multi cell scaffolds in sodium sulfate feed provided the ionic conductivity can be kept stable in anolyte when the pH drops below 2.

8.1 Program Highlights

- A NAS-D based electrochemical cell was operated at 25 mA/cm² in NaOH electrolyte for over 3000 hours. This cell performed at higher than 92 % sodium transport efficiency.
- The doped NAS-D membranes have showed excellent chemical stability in acidic (pH 0.6) as well as alkaline (pH 14) solutions. A NAS-D10 membrane was operated for over 1000 hours at 100 mA/cm² current density, the average driving voltage was 3 volts across a 0.7 mm thick membrane at 40^o C. The cell performed at a sodium current efficiency of 95 % in caustic feed.
- The new NaSICON series have exhibited high selectivity for sodium ions over hydronium ions and alkali ions, this provides the sodium sulfate recycling process using ceramic membranes an inherent advantage over competing technologies that rely on polymeric membranes.
- The performance of NaSICON membranes is not influenced by sparingly soluble species such as Mg²⁺, Ca²⁺, and Al³⁺ at an intermediate pH which precipitate in the polymeric membranes causing it to foul during electrochemical splitting of sodium sulfate salt cake.
- We have demonstrated at a laboratory scale that a NAS-G single membrane scaffold can be operated at higher than 90 % transport efficiency in complex alkaline feed at constant current density of 400 mA/cm². The driving voltage was 3.9 volts at 40^o C, across a 1.4 mm thick membrane.
- The new NaSICON membranes were operated in batch mode at 100, 200 300, and 400 mA/cm² in alkaline, acidic and caustic electrolytes.

- Electrochemical longevity of higher than 5000 hours at 25 mA/cm² was achieved in electrochemical test with the NaSICON membranes in caustic and alkaline electrolytes.
- The NaSICON membranes are 95 % selectivity for Na⁺ vs. Cs⁺, Sr⁺ & Al⁺.
- The dense ceramic membranes show no sign of electro osmotic transport of H₂O.
- The SO₄²⁺, Mg²⁺, Ca²⁺ Si⁴⁺, and Fe³⁺ ions will not transport across the ceramic membranes due to size and electroneutrality constraints
- The NaSICON structure restricts back diffusion of AlO²⁻, PO₄³⁻, and SO₄²⁻ ions present in waste sodium sulfate salt cake produced in the pulp and paper industry.

9.0

Suggested Future Work

The high sodium ion conductivity of the new NaSICON series provides an opportunity to produce high purity NaOH from sodium sulfate salt feed when the pH is greater than 2. Further work is needed to either improve the conductivity of NaSICON membranes in acidic electrolyte or arrest the exchange of H_3O^+ exchange at the membrane interface for generating caustic and weak acid from salt splitting of sodium sulfate salt cake.

Design and testing of a multi-cell stack with 5 x 5 inches NaSICON membranes is needed. Such stacks need to be operated in sodium sulfate as well as in chlorate feeds to evaluate long term performance characteristics. The economic merit of the electrochemical salt splitting process needs to be assessed and compared to present technology.

10.0

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- 3 "Energy Efficient Process for Recycling Waste Sodium Sulfate Utilizing Ceramic Solid Electrolytes", 1995 Annual Report-Phase 1 Contract DE-FC02-95CE41158.
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Appendix

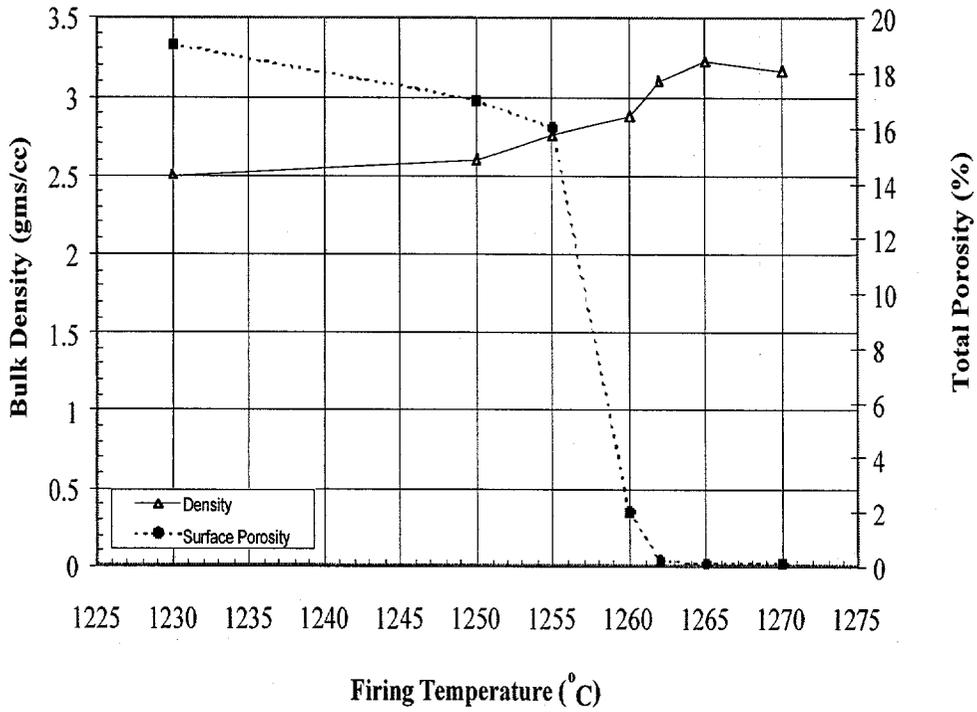


Figure 1: Sintering behavior of NaSICON Series 2

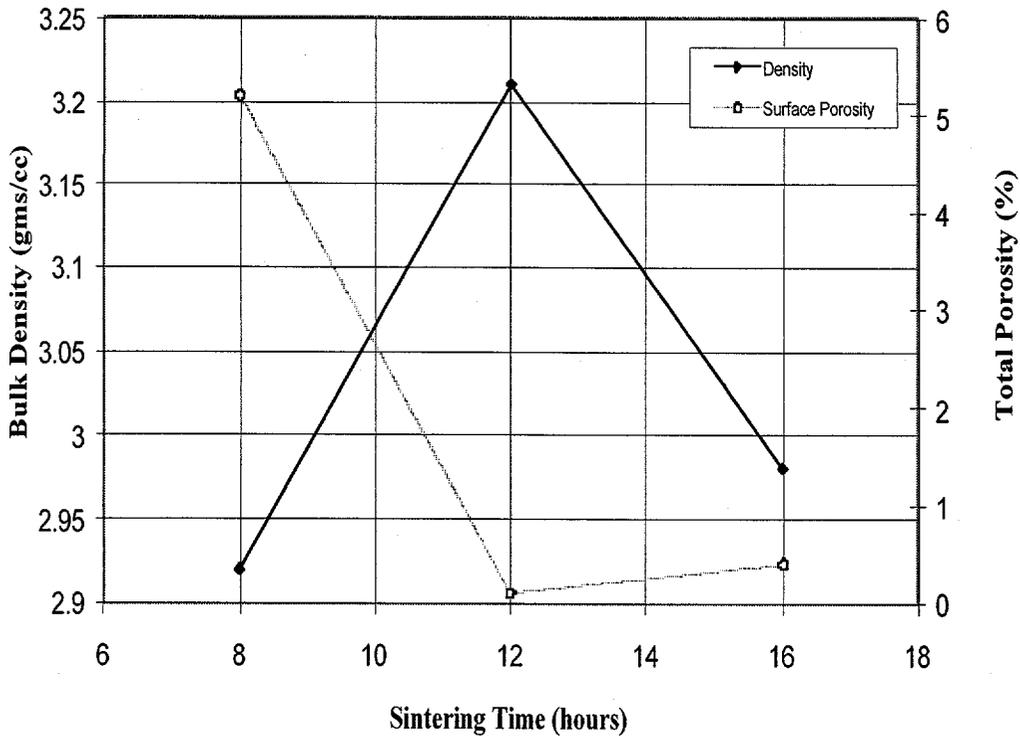


Figure 2: Sintering behavior of NaSICON Series 3

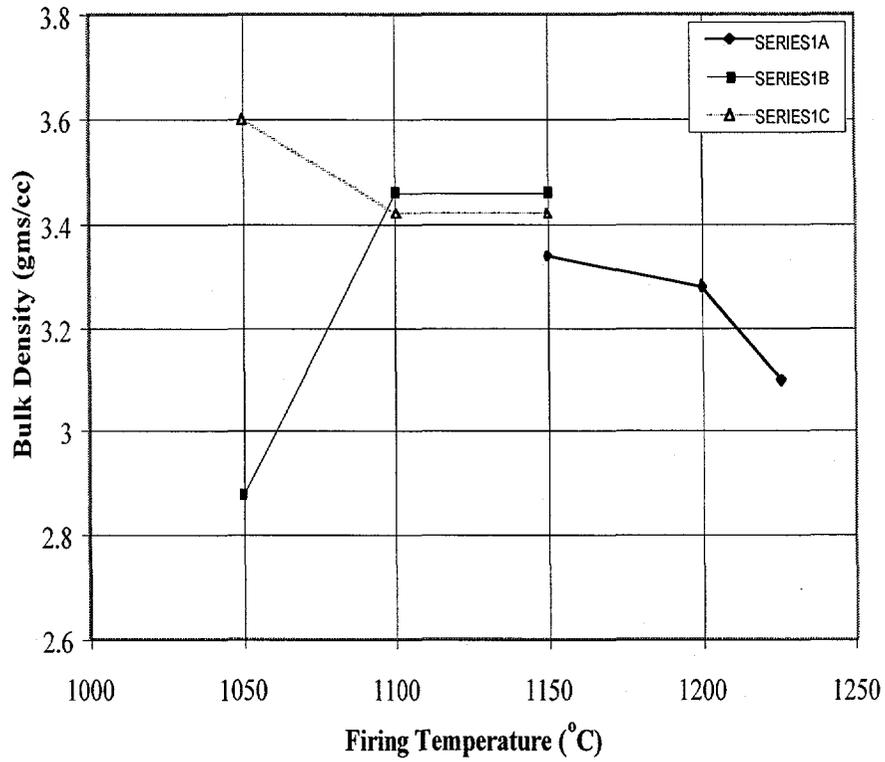


Figure 3: Sintering behavior of NaSICON Series 1

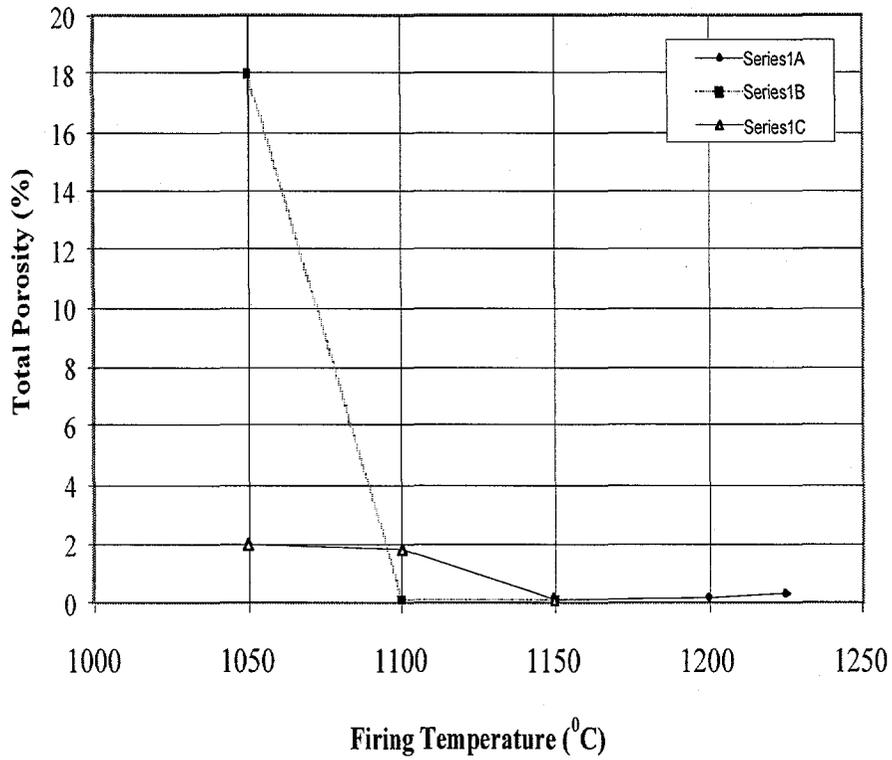


Figure 4: Sintering behavior of NaSICON Series 1

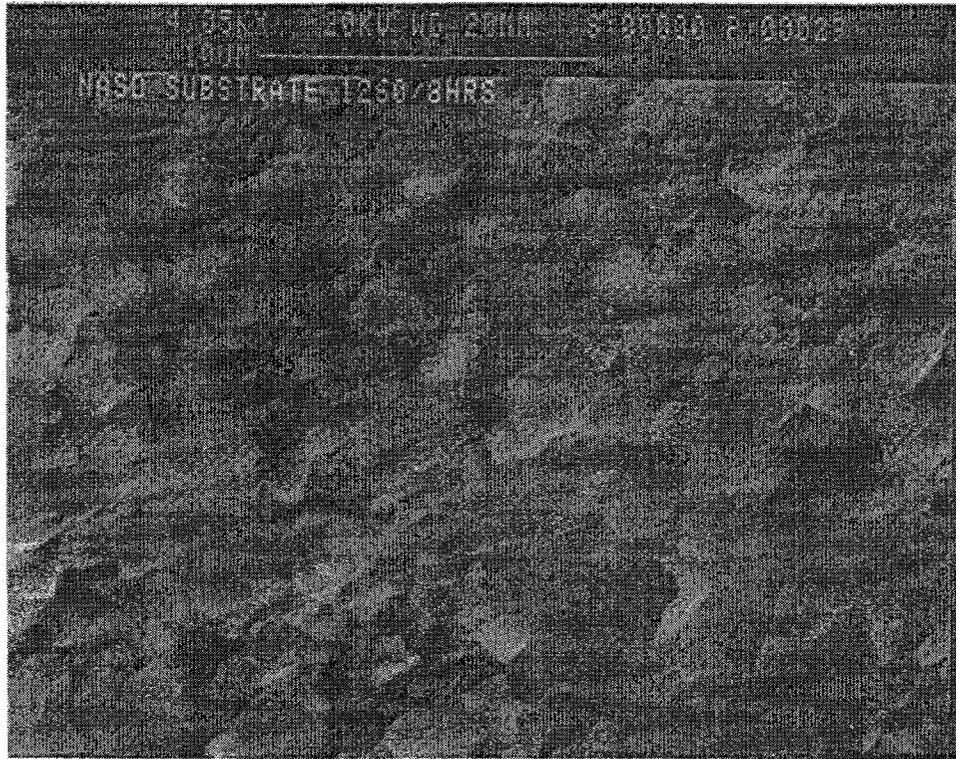


Figure 5: Fine grained microstructure of NASD membrane

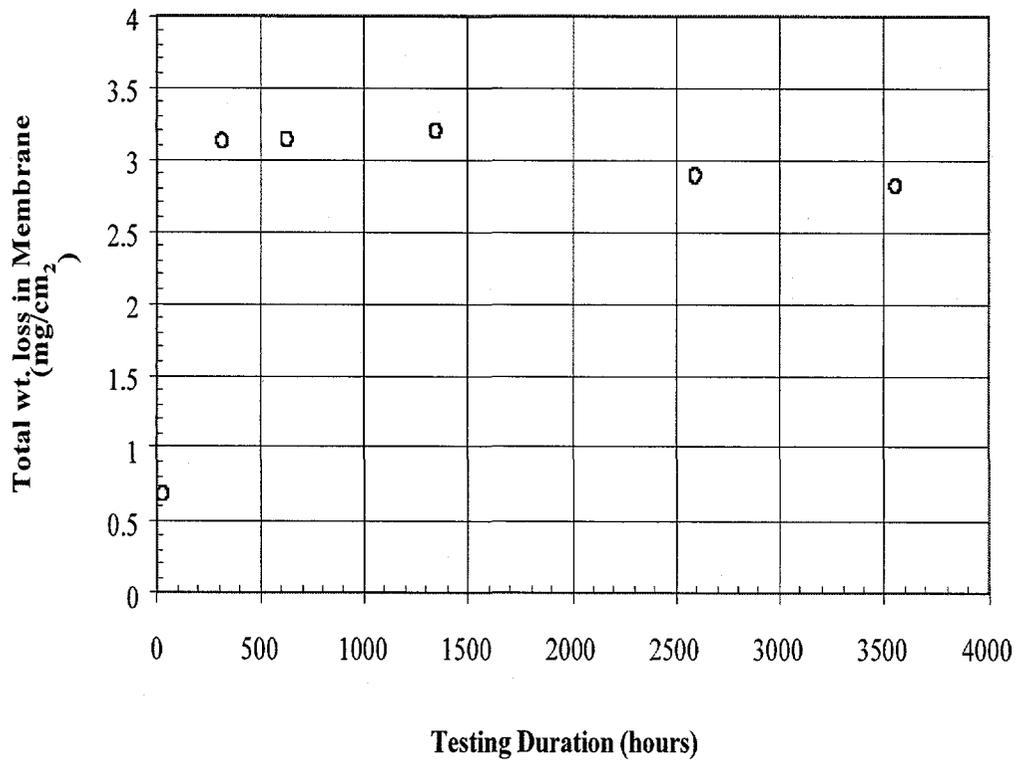


Figure 6: Chemical stability of NAS-A in 1M Na₂SO₄/1M H₂SO₄ (pH=2) at 60 ° C



Figure 7: NAS-A coating on NAS-D membrane

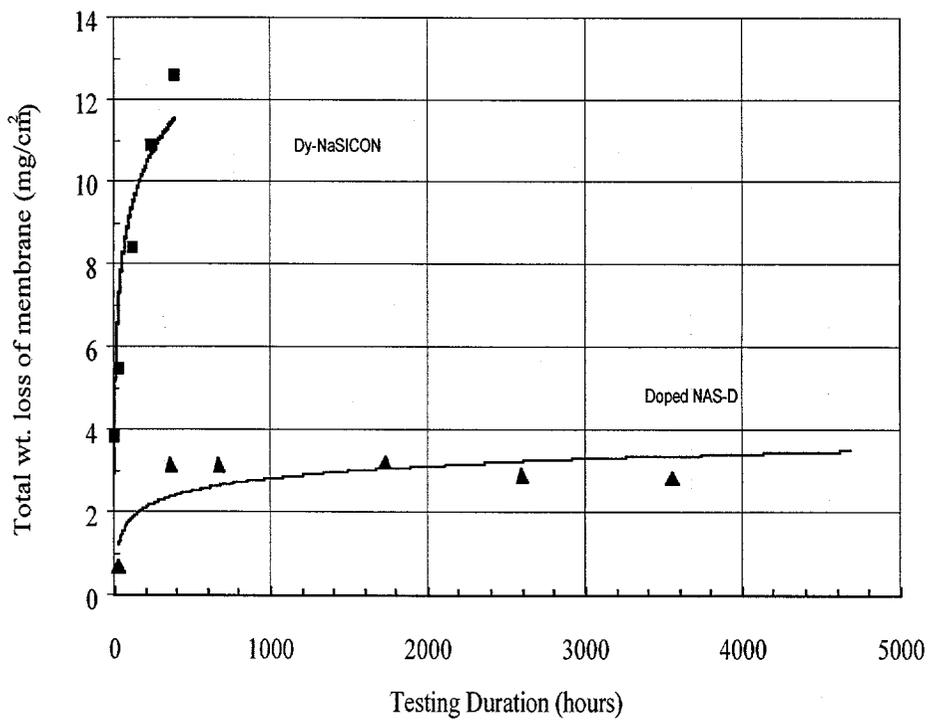


Figure 8: Chemical stability in 1M Na₂SO₄/1M H₂SO₄ (pH=0.2) at 60° C

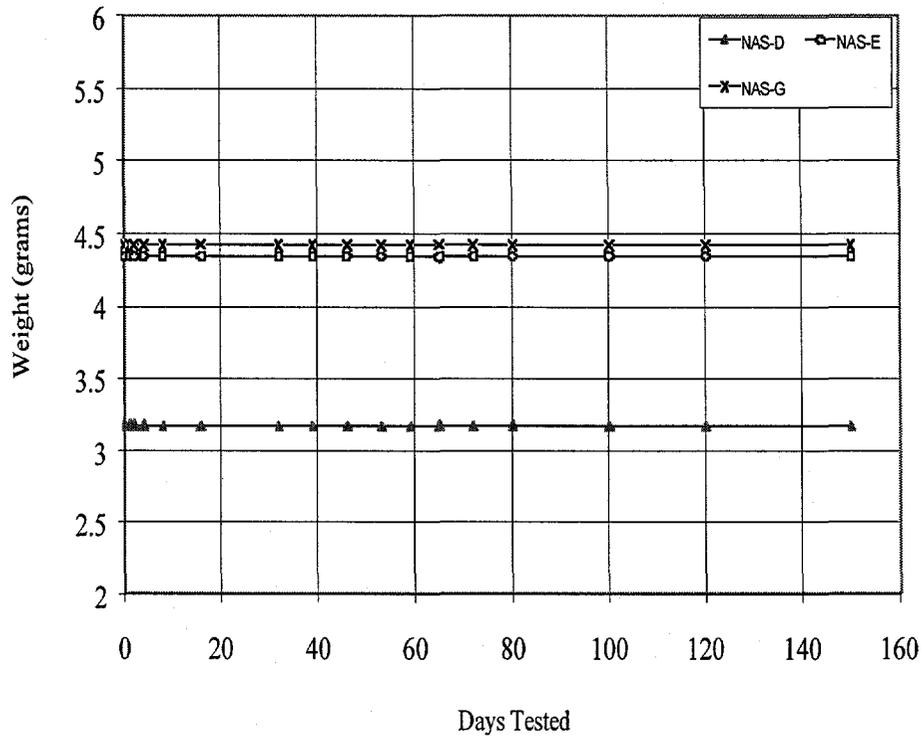


Figure 9: Chemical stability of NaSICON in 1.5 M NaOH @ 40° C

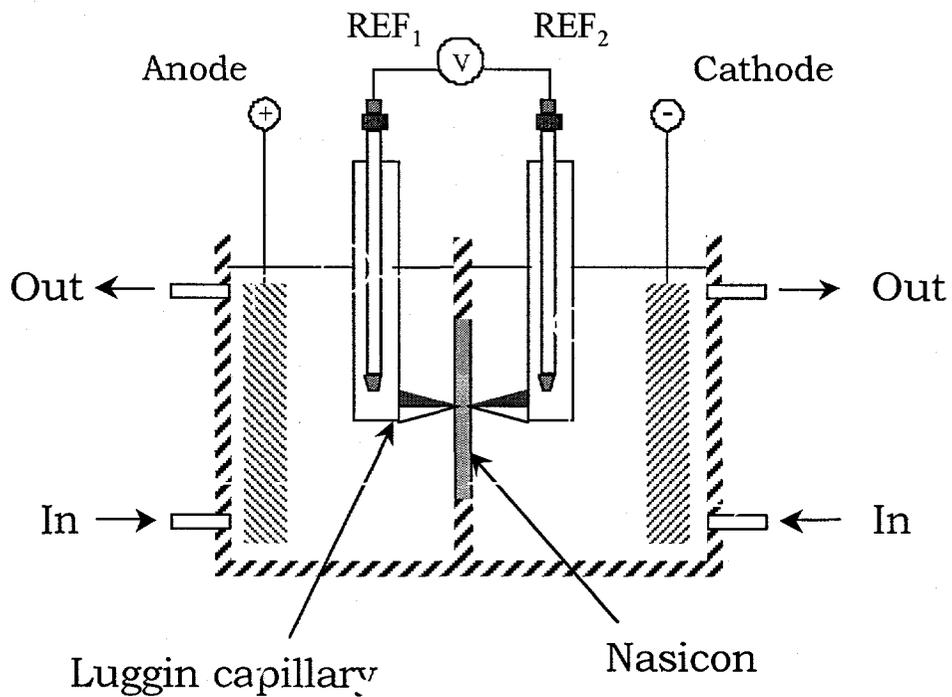


Figure 10: Four-Electrode electrochemical cell with NaSICON membrane

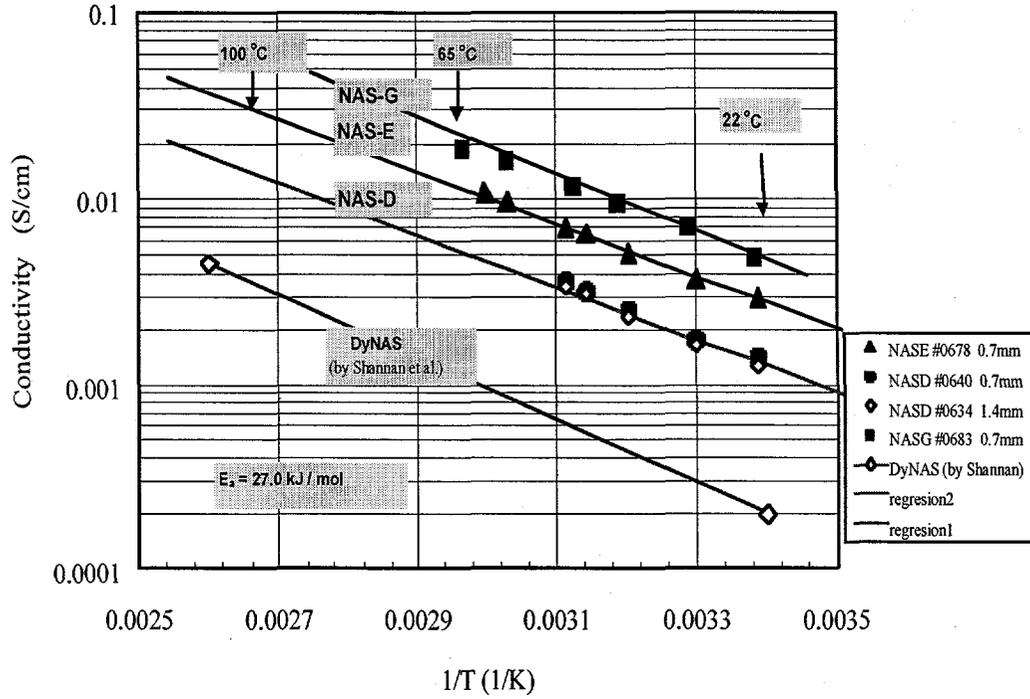


Figure 11: Conductivity of NaSICON membranes in 1.5 M NaOH @ 1.4 V/mm driving voltage across the membrane

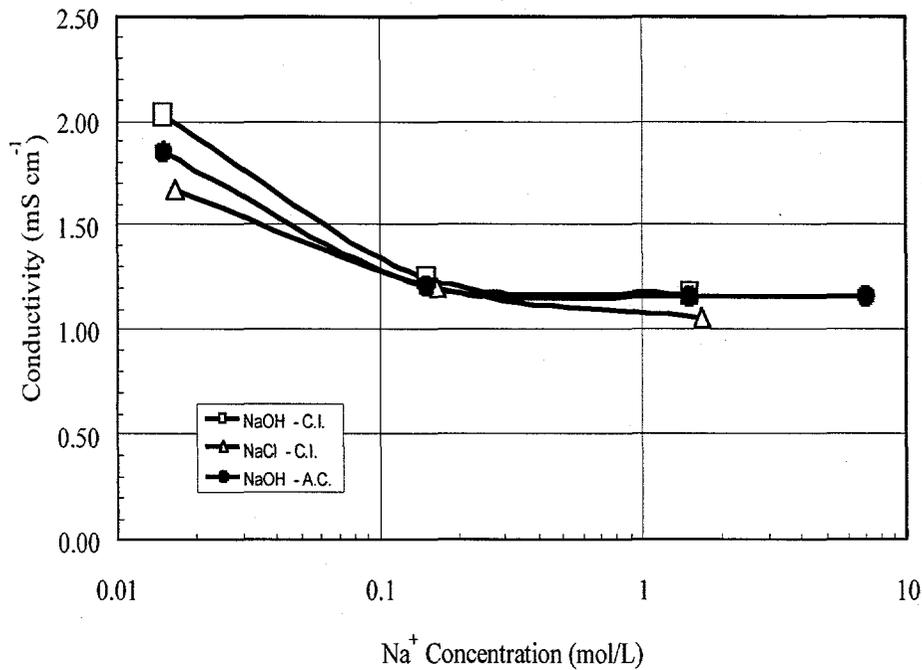


Figure 12: Conductivity of NASD # 0634 (d=0.14 cm, 3.29 cm²) in Na⁺ solutions by Current Interrupt and A.C. Impedance Technique @ 21° C

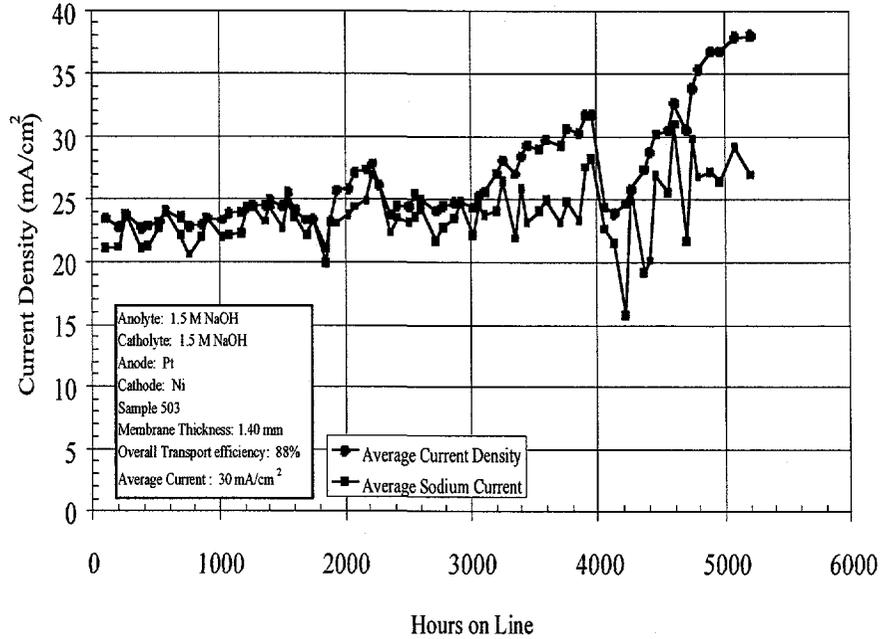


Figure 13: Performance of NAS-D10 in 1.5M NaOH, 4.5 volts and 40° C

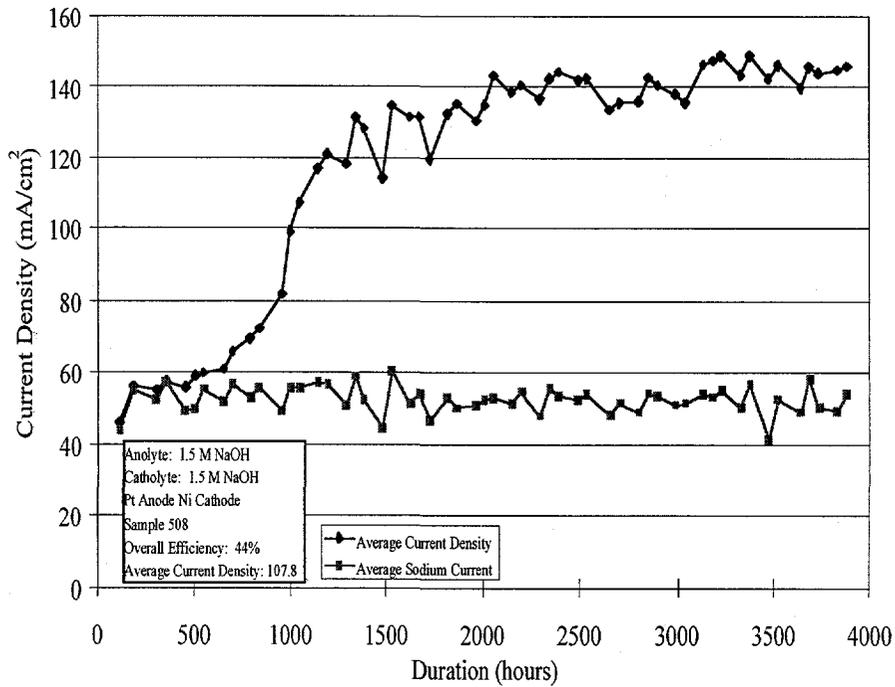


Figure 14: Performance of NAS-D50 in 1.5M electrolyte @ 4.5 V and 40° C

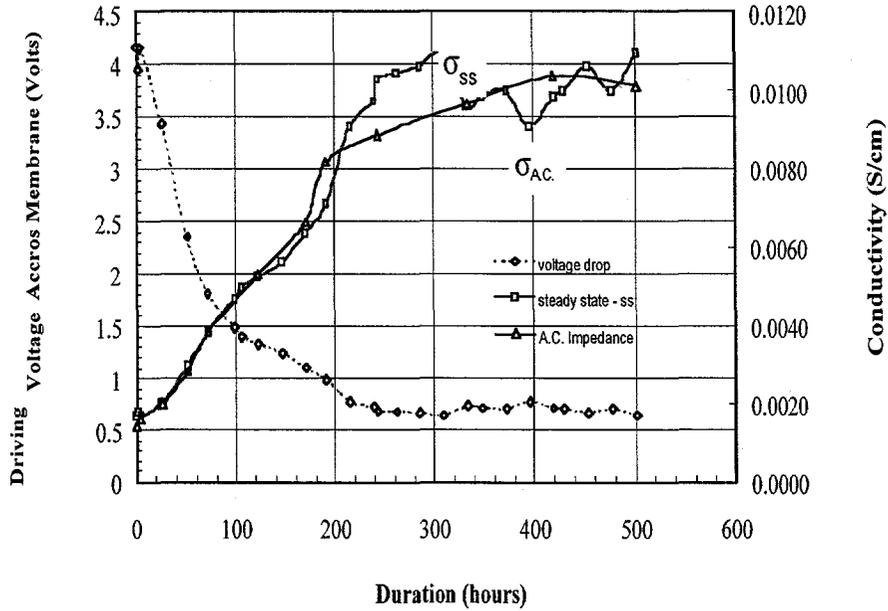


Figure 15: Performance of NAS-D membrane in 3M NaNO₃ + 2M NaOH solution @ 100 mA/cm² and 38±3° C (NASD # 0645, δ = 0.7 mm, S = 3.29 cm²)

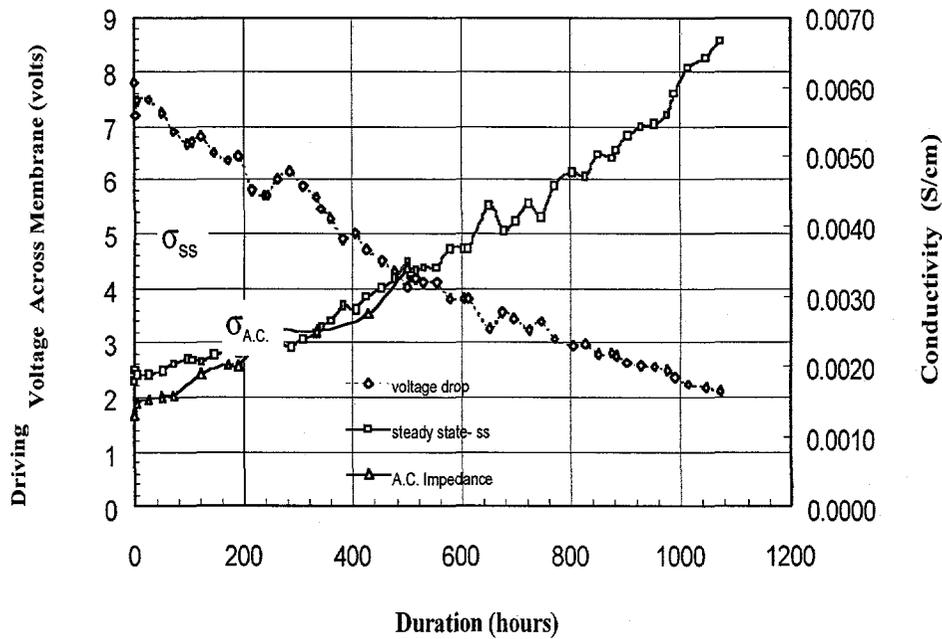


Figure 16: Performance of NAS-D10 membrane in 3M NaNO₃ + 2M NaOH solution @ 100mA/cm², 38±3° C, (# 0672, δ=1.4 mm, S = 3.29 cm²)

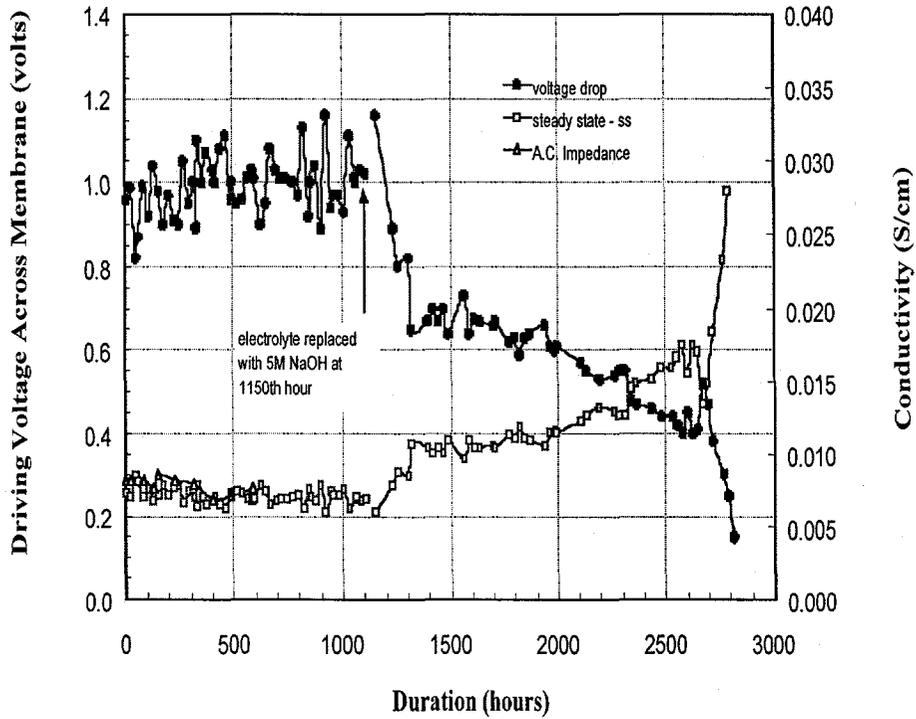


Figure 17: Performance of NAS-G membrane in 1.5M & 5M NaOH solution @ 100mA/cm² and 38+/-3° C, (NASG # 0684, $\delta=0.7$ mm, $S = 3.29$ cm²)

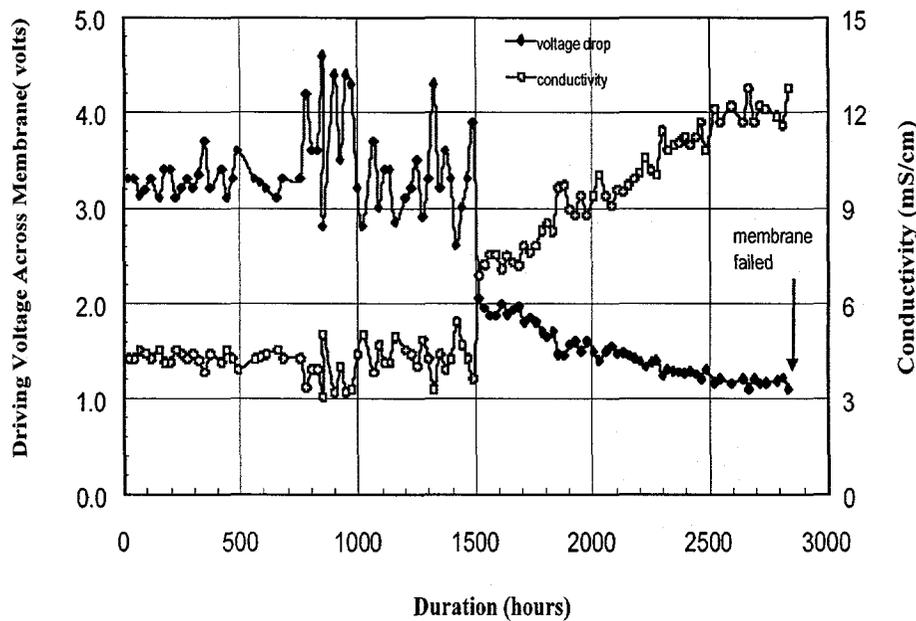


Figure 18: Performance of NAS-G membrane in 5M NaOH solution @ 200mA/cm² and 38+/-3° C, ($\delta=0.7$ mm, $S = 3.29$ cm²)

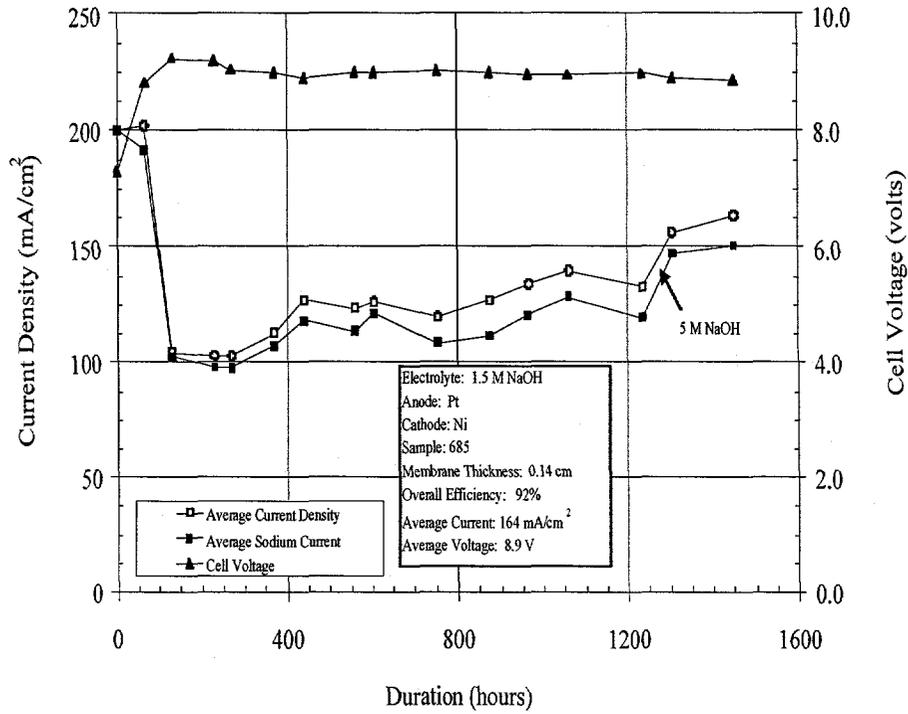


Figure 19: Electrochemical performance of NAS-G in 1.5M NaOH @ 40° C

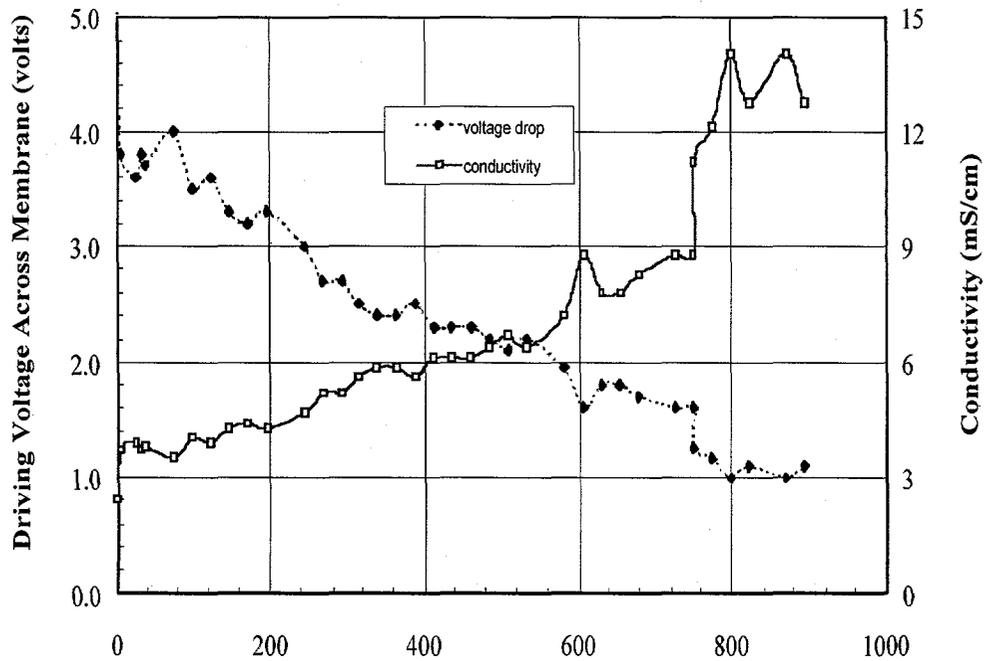


Figure 20: Performance of NAS-G10 membrane in 5M NaOH solution @ 200mA/cm² and 38±3° C, (NAS-G10 # 0780, $\delta=0.7$ mm, $S = 3.29$ cm²)

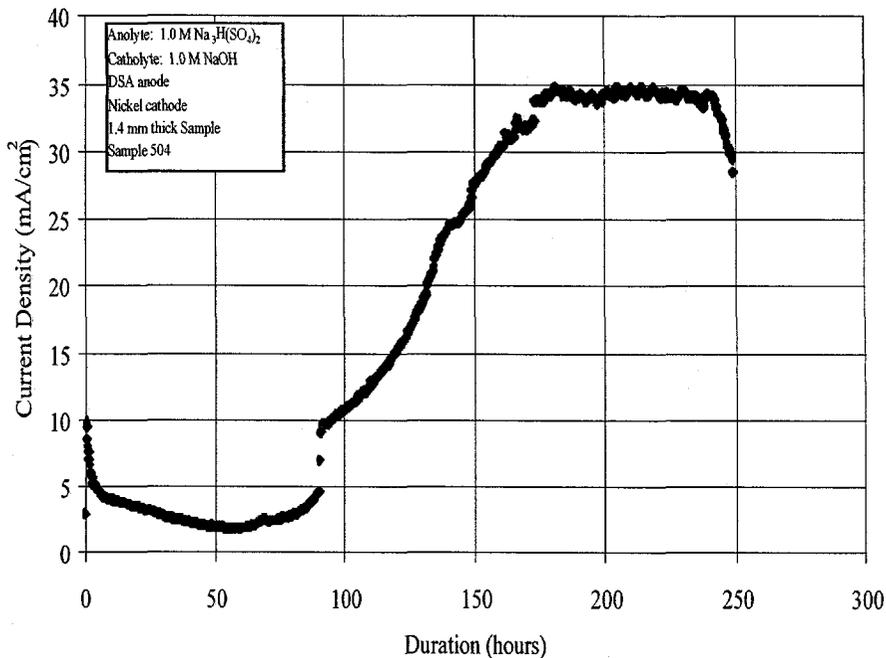


Figure 21: Electrochemical performance of NASD-10 in 1M $\text{Na}_2\text{H}(\text{SO}_4)_2$ anolyte current vs. time @ 4.5 volts and 40° C

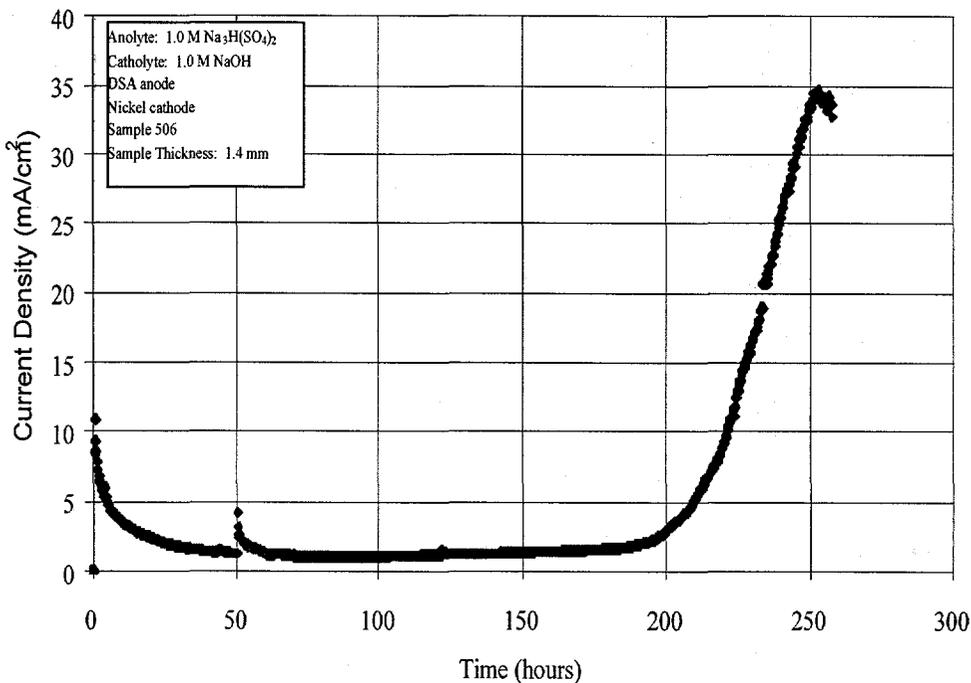


Figure 22: Electrochemical performance of NAS-D25 in 1M $\text{Na}_2\text{H}(\text{SO}_4)_2$ anolyte current vs. time @ 4.5 volts and 40° C

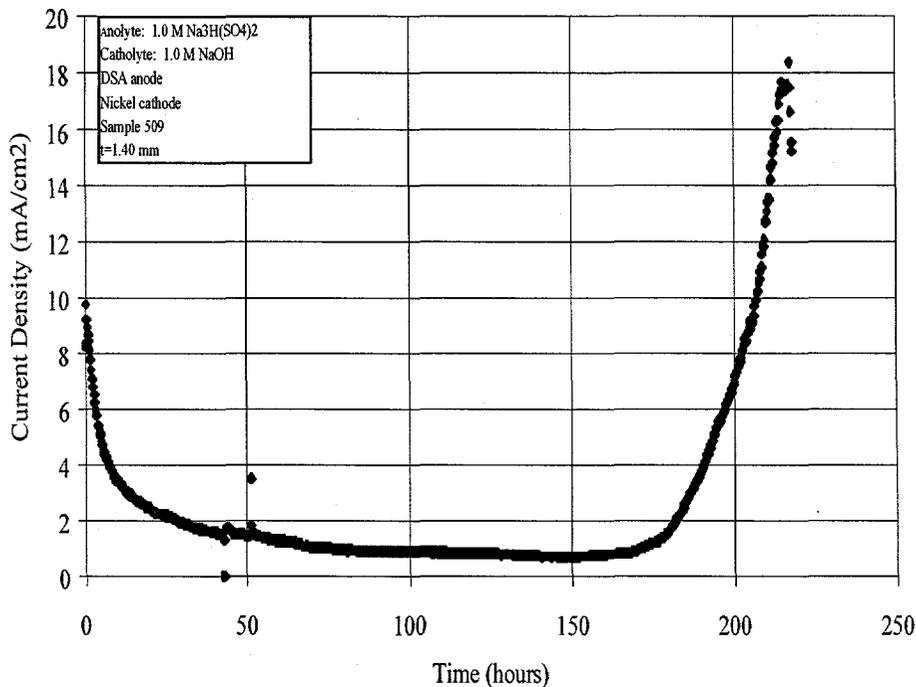


Figure 23: Electrochemical performance of NAS-D50 in 1M $\text{Na}_2\text{H}(\text{SO}_4)$ anolyte current vs. time @ 4.5 volts and 40° C

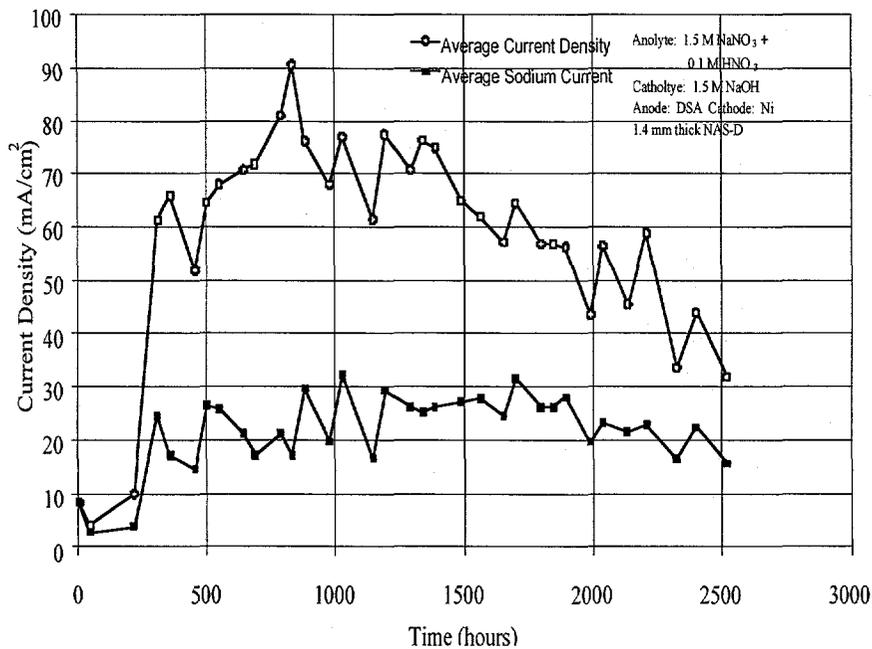


Figure 24: Electrochemical performance of NAS-D in 1M $\text{NaNO}_3/\text{HNO}_3$ anolyte @ pH=1.10, and 40° C

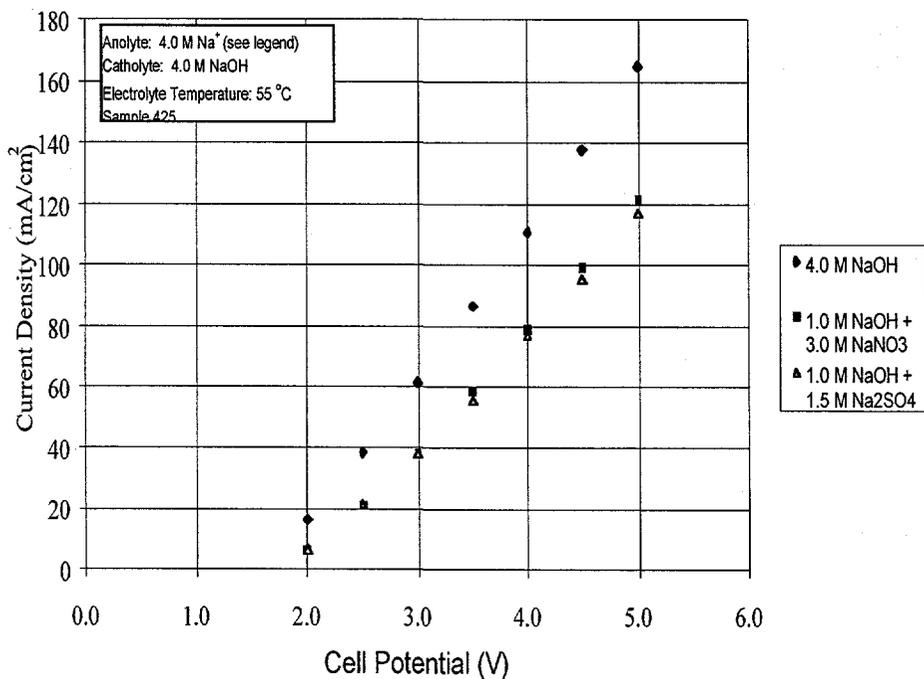


Figure 25: Effect of OH⁻, NO₃⁻, and SO₄²⁻ ions on conductivity (NAS-D, 0.7 mm)

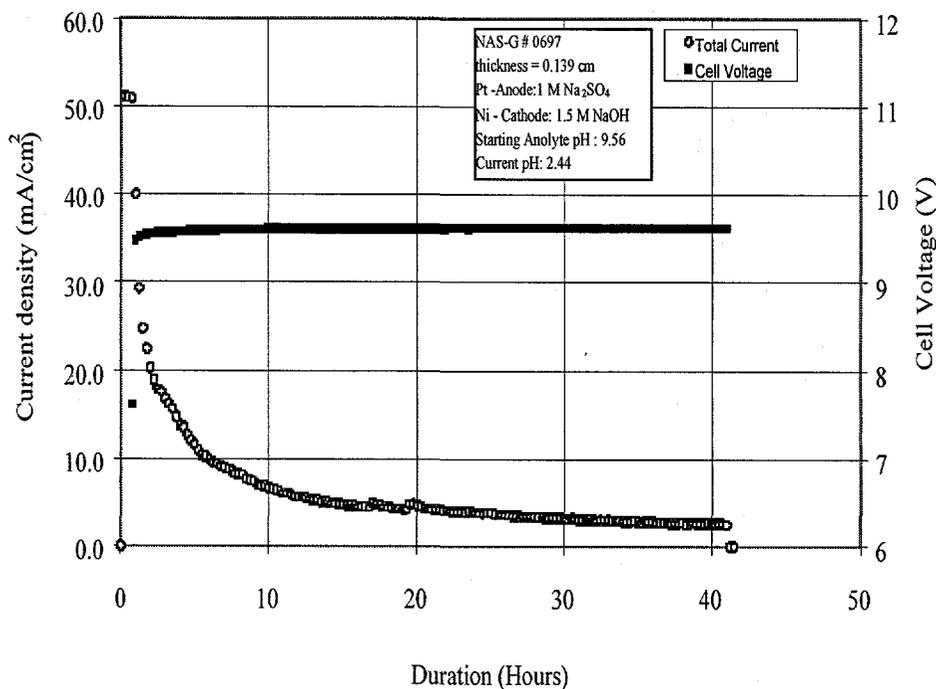


Figure 26: Electrochemical performance of NAS-G in 1M Na₂SO₄ at 22o C

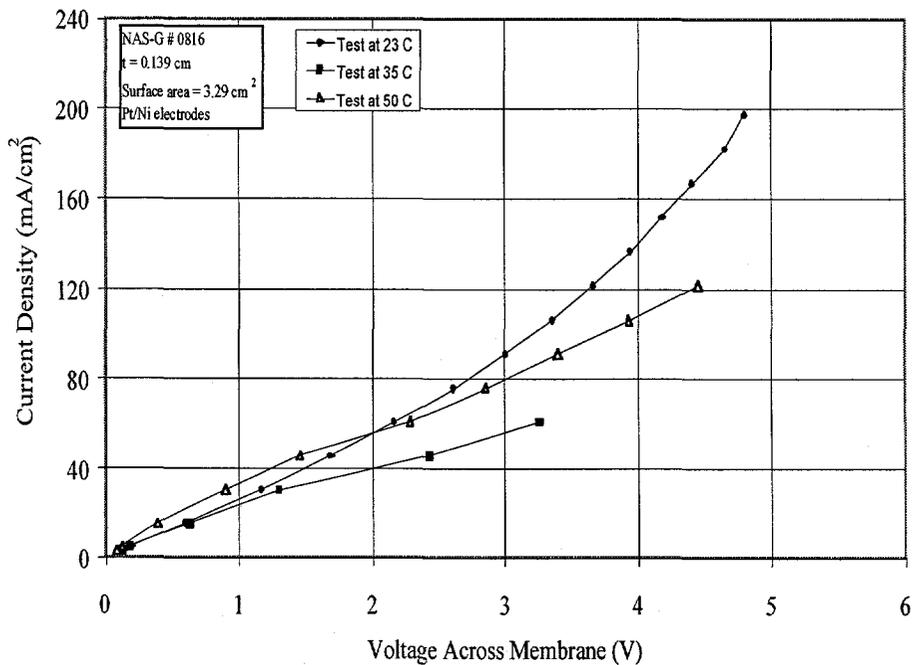


Figure 27: I vs V performance of NAS-G in 1M Na₂SO₄/1.5M NaOH