

Impedance characteristics of a rotating disc electrode coated with a sulfonated polysulfone cation-exchange membrane

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Abstract

The transport of sodium ions through a sulfonated polysulfone (SPSF) cation-exchange membrane coated on a rotating disc electrode is investigated by means of cyclic voltammetry (CV) and a.c. impedance spectroscopy. Impedance plots are analyzed by a non-linear least-squares fitting method. The transport (diffusion coefficient), interfacial parameters (double layer capacitance), and total resistance of the SPSF membrane coated electrodes are investigated as the function of sulfonic acid group concentration in the SPSF membrane, membrane thickness, electrolyte concentration, and reduction potential. The diffusion coefficients are found to vary between 1.082×10^{-12} and $1.136 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ as the sulfonic acid group concentration is increased from 0.672 to 1.18 mmol/g membrane at open circuit voltage. The double-layer capacitance depends on electrolyte concentration and reduction potential, and sulfonic acid group concentration, but not on the membrane thickness. The total resistance depends on sulfonic acid group concentration, electrolyte concentration, membrane thickness, and reduction potential. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: a.c. impedance spectroscopy; Cyclic voltammetry; Diffusion coefficient; Double layer capacitance

1. Introduction

There is a great demand for chemically stable, ion-exchange membranes for electro-membrane processes, such as electrodialysis and polymer electrolyte fuel cells. Up to now, only a few chemically stable ion-exchange polymers that withstand the aggressive reaction conditions of some electro-membrane processes (high acidic and/or strongly oxidizing environment) have been commercially available, such as Nafion[®] or Flemion[®]. Nafion[®] has a high price, however, which hinders the increased commercial application of electro-membrane processes.

The essential properties of the membrane for electrochemical applications include good permselectivity, high ionic conductivity, no electronic conductivity, adequate chemical and thermal stability, and sufficient mechanical

strength under operating conditions. Electrodes coated with thin polymer films have become the subject of considerable research [1–4]. Investigations of membrane-type coatings are of general technological relevance. For example, the performance of corrosion-protection coatings is determined by the permeability and the interfacial behaviour of the films, which can be investigated with permeable model coatings on electrodes [5,6]. Membrane equilibria, including selectivity properties, can be derived conveniently from electrochemical experiments with coated electrodes. For instance, transport process through membrane coated electrodes have been studied using steady-state, limiting-current measurements. Also, ion-exchange properties of polymer coatings have been studied [5–9] using conventional electrochemical methods.

The impedance technique is very suitable for the investigation of electrode processes. In the field of polymer-coated electrodes, this technique has been used mostly to study mass transport through the porous layer on the electrode [10,11].

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In this work, a cation-exchange membrane was prepared by the sulfonation of the chemically stable polymer, polysulfone Udel®. The resulting sulfonated polysulfone membranes have been characterized in terms of ion-exchange group content and transport (diffusion coefficient), interfacial parameters (double layer capacitance), and total resistance have been investigated by means of a.c. impedance spectroscopy.

2. Experimental

2.1. Chemicals and solutions

NaCl (Junsei Chemical, Japan) was used as received. The electrolytes consisted of 0.005 to 0.5 M NaCl. All electrolytes were prepared with triple-distilled water and de-aerated by passing nitrogen. All experiments were carried out at room temperature ($20 \pm 0.5^\circ\text{C}$).

2.2. Preparation and properties of sulfonated polysulfone

The sulfonated polysulfone (SPSF) was prepared by the following method [12,13]. First, trimethyl chlorosilane, used as mediate, and chlorosulfuric acid, used as sulfonating agent, were introduced into the main chain of polysulfone for formation of sulfone groups. By changing the stoichiometric ratio of chlorosulfuric acid and polysulfone, sulfonated polysulfone with various concentrations of the sulfonic acid (SO_3H) group was obtained.

The SO_3H group concentration was determined from measurement of the total ion-exchange capacity by titration. The membrane was converted into the H-form with 0.1 M hydrochloric acid. The membrane was removed from the solution and rinsed overnight in distilled water.

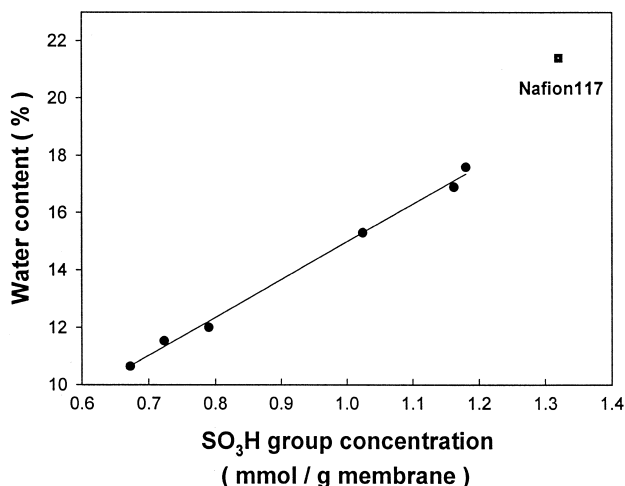


Fig. 1. Water content vs. SO_3H group concentration.

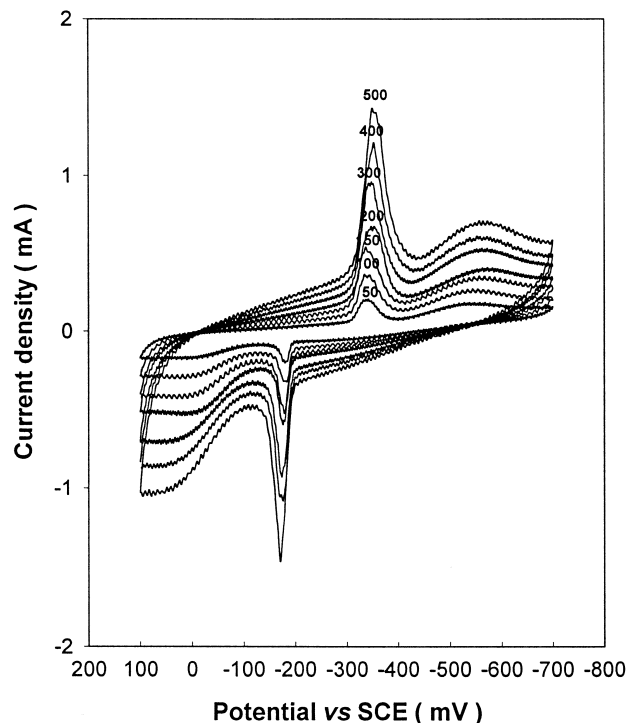


Fig. 2. Cyclic voltammograms for SPSF membrane coated electrode in 0.5 M NaCl electrolyte; rotation rate of electrode = 1500 rpm; sulfonic acid group concentration = 1.18 mmol/g membrane; geometric electrode area = 0.2826 cm^2 ; membrane thickness = 2 μm .

Subsequently, the H-form membrane was immersed in 2 M NaCl aqueous solution at 298 K for 24 h and the hydrogen ions liberated from the membrane were titrated with 2 M NaOH aqueous solution.

2.3. Cell and electrodes

A conventional three-electrode cell was used, with a platinum wire counter electrode and KCl-saturated calomel reference electrode (SCE). The working electrode was a platinum disk (geometric area 0.2826 cm^2) embedded in a Teflon holder and coated with SPSF membrane. The working electrode was mechanically polished with aluminium oxide paper (# 0.1 μm), chemically etched in 30% HNO_3 , and rinsed in distilled water. Thin membranes of SPSF were deposited on the surface of a rotating disc electrode (RDE) by spin-coating at a rotation rate of 2000 rpm. The dry membrane thickness was measured with a thickness gauge (Peacock, Ozaki, Japan) and was 1 to 9 μm .

2.4. Instrumentation and procedure

A potentiostat–galvanostat PAR 273 system and a frequency analyzer were used with a PAR 5210 lock-in-amplifier. Frequency sweeps were made from 100 KHz to 8.85 mHz using a sinusoidal voltage amplitude of 5 mV.

Table 1
Peak potentials of SPSF membrane coated electrode

Scan rate (mV s ⁻¹)	E _{pa}	E _{pc} (mV vs. SCE)	E _{1/2}
50	-180	-342	-261
100	-184	-334	-259
150	-178	-338	-258
200	-176	-348	-262
300	-174	-348	-261
400	-176	-352	-264
500	-170	-350	-260

The SPSF membrane coated electrodes were immersed in the desired NaCl electrolyte for at least 12 h.

3. Results and discussion

3.1. Properties of sulfonated polysulfone

The water content of various sulfonic acid groups containing the SPSF membranes is shown in Fig. 1. Hydrophilicity of the membrane is essential because it enables the transport of counter ions. The water content of the SPSF membrane increases with increasing concentration of the sulfonic acid group. The water content of the SPSF membrane is lower than that of a Nafion 117 membrane.

3.2. Cyclic voltammetry

Cyclic voltammetry is one of the most useful techniques for investigating electrochemical reactions. Typical cyclic voltammograms for the SPSF membrane coated electrodes in 0.5 M NaCl electrolyte at a rotation rate of 1500 rpm are presented in Fig. 2. These cyclic voltammograms reflect the ion-exchange reactions of sulfonic acid groups and counter ions. Such curves were recorded before and

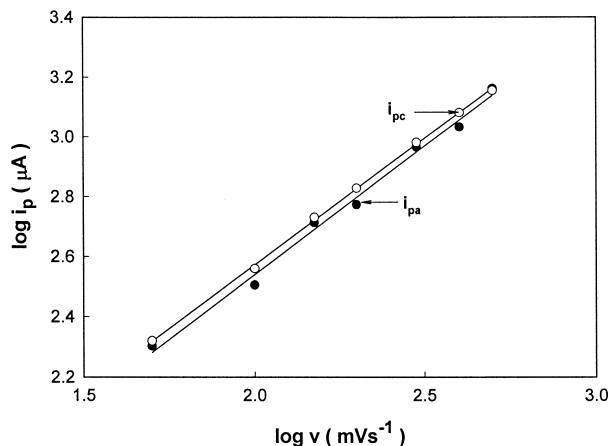


Fig. 3. Relationship between peak current, i_p , and scan rate, ν , for cyclic voltammograms.

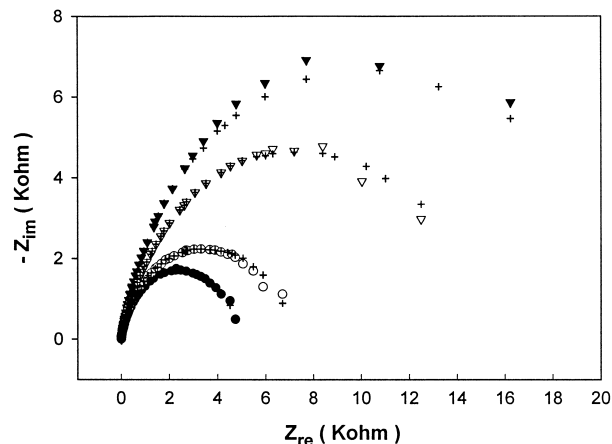


Fig. 4. Complex impedance plots obtained for SPSF membrane coated electrode at various SO₃H group concentrations in 0.5 M NaCl electrolyte: (●) 1.18, (○) 1.024, (▽) 0.79, (▼) 0.672 mmol/g membrane. (+) simulation curve. Membrane thickness: $\approx 1.0 \mu\text{m}$. Rotation rate of electrode = 1500 rpm.

after the a.c. impedance measurements as a check of electrode condition. The anodic and cathodic current peaks are symmetrically shaped irrespective of the scan rate, ν , over the range 50 to 500 mV s⁻¹ and increased with scan rate. The peak potentials, E_p, of the SPSF membrane coated electrodes shown in Fig. 2, are listed in Table 1.

Typical i_p - ν relationships obtained from Fig. 2 are given in Fig. 3. Good linearity is observed over the scan rate range 50 to 500 mV s⁻¹. In a surface wave ($x = 1$), i_p is proportional to ν , and in a diffusion-controlled wave ($x = 0.5$), i_p is proportional to $\nu^{1/2}$. The x -value reflects the mobility of ionic species in the SPSF membrane matrix. In order words, when $x = 1$, the mobility of ionic species is high, but when $x = 0.5$, that of ionic species is low [14]. From Fig. 3, the x -values of the cathodic and anodic peak currents are 0.8454 and 0.8613, respectively. Thus, it is concluded that the mobilities of the sodium ions in the SPSF membrane coated electrodes are high.

3.3. Impedance spectroscopy measurements

Impedance spectroscopy measurements were conducted to characterize the SPSF membrane coated on the RDE as the function of sulfonic acid concentration, membrane

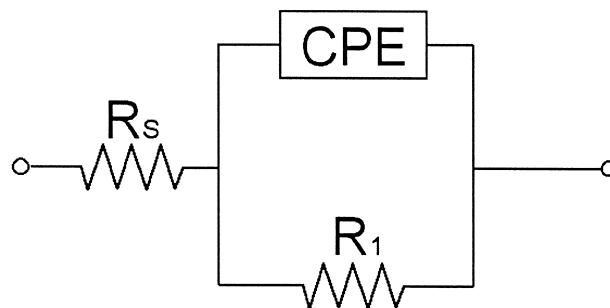


Fig. 5. Equivalent circuit for SPSF membrane coated electrode.

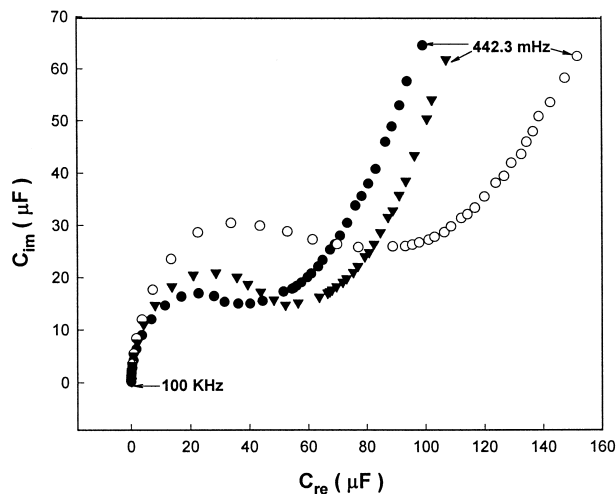


Fig. 6. Complex plane plots of capacitance for SPSF membrane coated electrodes in 0.5 M NaCl electrolyte: (●) 1.062, (▼) 0.79, (○) 0.672 mmol/g membrane. Rotation rate of electrode = 1500 rpm. Membrane thickness = 1 μm .

thickness, electrolyte concentration, and reduction potential. Also, determination was made of the total impedance of the electrode coated with SPSF membranes with varying SO_3H group concentrations.

Complex plane impedance plots obtained on the SPSF membrane coated electrode are shown in Fig. 4 as a function of the sulfonic acid concentration in 0.5 M NaCl electrolyte at open-circuit. The absence of any semicircular arc at high frequencies implies that heterogeneous electron transfer at the electrode-membrane interface is rapid and that the membrane resistance is low [15]. The total resistance decreases with increasing SO_3H group concentration.

A non-linear least-squares analysis (NLLS) was performed to fit the impedance of the equivalent circuit to the data [16]. The equivalent circuit of the SPSF membrane coated electrodes employed in this study is illustrated in

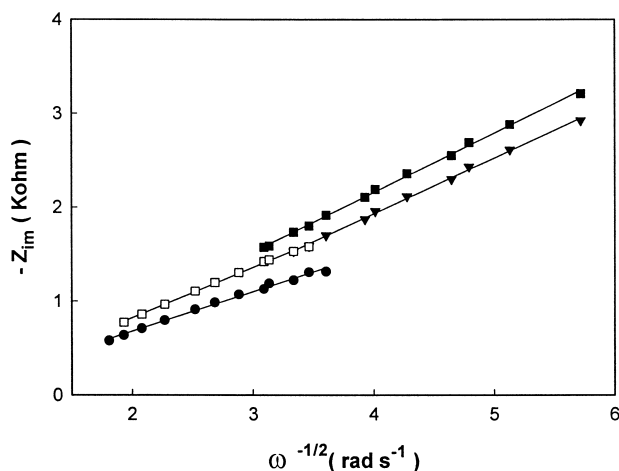


Fig. 7. Imaginary parts of complex impedance plot vs. $\omega^{-1/2}$: (●) 1.18, (□) 1.024, (▼) 0.723, (■) 0.672 mmol/g membrane. Membrane thickness = 1 μm .

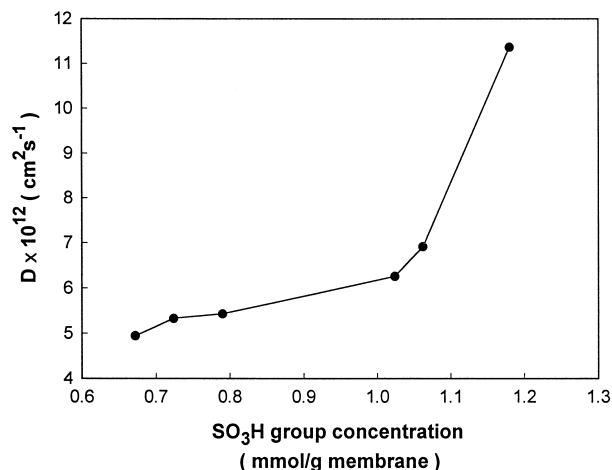


Fig. 8. Diffusion coefficient vs. SO_3H group concentration in 0.5 M NaCl electrolyte. Rotation rate of electrode = 1500 rpm. Membrane thickness = 1 μm .

Fig. 5. The equivalent circuit consists of R_s , R_1 and CPE, connected as shown in Fig. 5; R_s and R_1 represent the electrolyte resistance and the resistance related to the polymer resistance and the redox reaction resistance, respectively. The total resistance is $R_s + R_1$. The impedance of the constant phase element is given by [17]:

$$Z_{\text{CPE}} = (j\omega)^{-n} Q \quad (1)$$

and

$$1/Q = (1/R_s)^{1-n} C \quad (2)$$

where: Q is a constant representative of CPE; ω is the angular frequency; n is a dimensionless parameter, between zero and unity, which is a measure of the rotation of the impedance spectrum in the complex-plane given by $90^\circ(1-n)$; C is the capacitance.

The resulting curves from fitting parameters in Fig. 4 show that the simulation curve is in quite good agreement with the experimental impedance data.

Complex plane plots of capacitance in 0.5 M NaCl electrolyte and 1500 rpm are shown in Fig. 6. The complex plane plot of capacitance shows one well-defined semicircle and the values of the double-layer capacitance, C_{dl} , are calculated from these plots. C_{re} and C_{im} are the real and imaginary components, respectively. The double-

Table 2

Values of parameters of equivalent circuit obtained from fitting experimental data: membrane thickness dependence in 0.5 M NaCl electrolyte at open circuit. Rotation rate of electrode = 1500 rpm

Membrane thickness (μm)	R_s (Ω)	R_T (Ω)	$Q \times 10^4$ (mho)	n	C_{dl} (μF)	$D \times 10^{12}$ ($\text{cm}^2 \text{s}^{-1}$)
1	6.73	7664	0.8981	0.8044	37.22	2.5642
2	18.88	10878	1.2525	0.83658	42.35	2.9659
3.5	28.77	18800	1.1761	0.7623	39.44	3.6378
9	32.28	23416	1.3792	0.79037	42.77	5.1257

Table 3

Values of parameters of equivalent circuit obtained from the fitting of experimental data: electrolyte concentration dependence at open circuit. Rotation rate of electrode = 1500 rpm. Membrane thickness = 1 μm . Sulfonic acid group concentration = 1.024 mmol/g membrane

Concentration (mole/l)	R_S (Ω)	R_T (Ω)	$Q \times 10^4$ (mho)	n	C_{dl} (μF)	$D \times 10^{12}$ ($\text{cm}^2 \text{s}^{-1}$)
0.005	285.15	97424	1.2512	0.7303	73.85	2.4598
0.01	177.24	92474	1.0245	0.7052	62.35	2.3372
0.05	22.096	48211	1.5081	0.78389	47.29	2.87977
0.1	17.096	42204	1.3529	0.7646	45.39	3.17776
0.5	5.299	5928.6	1.1579	0.84055	43	6.9098

layer capacitance decreases with increasing SO_3H group concentration.

The general solution for a.c. impedance due to diffusion in a thin film has been given by Ho et al. [18], and by Armstrong [19]. From an electric point of view, the behaviour is equivalent to that of a finite transmission line. At high frequencies ($\omega \gg D/l^2$), the limiting behaviour is equivalent to that of a Warburg impedance plot, i.e., a linear (45°) branch in the complex plane plot, given by:

$$Z_D = \sigma \omega^{-1/2} (1 - j) \quad (3)$$

where, at equilibrium potential:

$$\sigma = 2\sqrt{2} RT/n^2 F^2 D^{1/2} C^0 \quad (4)$$

where: C^0 is the concentration of the diffusing species; n is the number of electrons involved in the electrochemical processes; R , T , and F have their usual meaning. The diffusion coefficient in the high-frequency domain, D , can be readily determined in the semi-infinite range by applying Eqs. (3) and (4) to the points on the 45° linear branches. The imaginary part of the impedance is proportional to $\omega^{-1/2}$, as shown in Fig. 7. The Warburg coefficient, σ , slightly decreases with increasing SO_3H group concentration. The dependence of the diffusion coefficient

on SO_3H group concentration is given in Fig. 8. The diffusion coefficients, D , vary from 1.082×10^{-12} to $1.136 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ as the sulfonic acid group concentration is increased from 0.672 to 1.18 mmol/g membrane, at the open-circuit potential. Rubinstein et al. [20] reported that the apparent diffusion coefficient of sodium ions for the system Pt/Nafion, $\text{Ru}(\text{bpy})_3^{3-/2-}$ (using a model which assumes two parallel diffusion paths in the film and with values obtained by curve fitting to experiments) are $D_1 = 1.5 \times 10^{-10}$ and $D_2 = 2.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. Hence, in this case, the diffusion coefficients in the SPSF membrane system are about an order of magnitude smaller than the diffusion coefficients in the Nafion film.

The dependence of the total resistance, diffusion coefficient, and double-layer capacitance on membrane thickness and electrolyte concentration is given in Tables 2 and 3. From Table 2, the total resistance and diffusion coefficient increase but the double-layer capacitance at the electrode-membrane interface displays no dependence on the membrane thickness. From Table 3, the diffusion coefficient increases but the total resistance and double-layer capacitance decrease with increasing electrolyte concentration. At larger polarizations (highly charged electrode) or with more concentrated electrolytes, the charge in electrolyte solution becomes more tightly compressed against the boundary at the outer Helmholtz plane in metal-membrane interface [21]. Hence, as the electrode becomes more highly charged, the diffuse layer should become more compact and C_{dl} should rise. As the electrolyte concentration rises, there should be a similar compression of the diffuse layer and a consequent rise in capacitance.

After applying various reduction potentials to the SPSF membrane system, the total resistance and capacitance were measured, see Fig. 9. At potentials less than -330 mV, the total resistance decreases, while at potentials more than -370 mV, the total resistance increases with increasing potential. Thus, low and high values of total resistance can be expected to correspond to high and low current

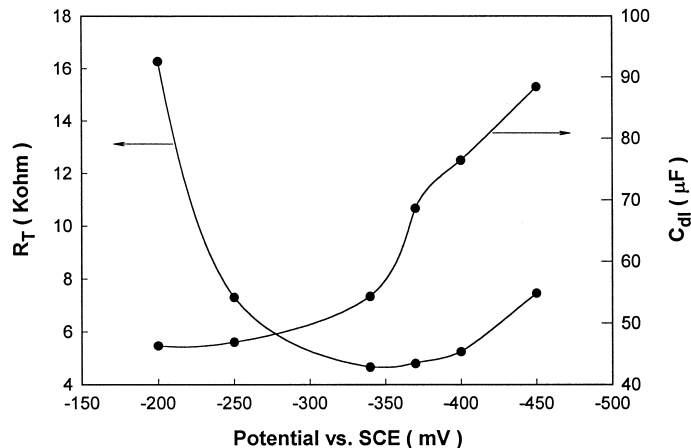


Fig. 9. Total resistance and double-layer capacitance of SPSF membrane coated electrodes as a function of reduction potential in 0.5 M NaCl electrolyte. Rotation rate of electrode = 1500 rpm. Membrane thickness = 6 μm .

values in cyclic voltammograms (Fig. 2). When an external potential is applied to the membrane system, counter ions transfer from the bulk electrolyte to the sulfonic acid groups attached to the membrane and completely oxidized sulfonic acid groups will be insulators. This phenomena is consistent with the findings of other studies [11].

4. Conclusions

The transport of sodium ions through a SPSF cation-exchange membrane coated on a rotating disc electrode has been investigated by using cyclic voltammetry (CV) and a.c. impedance spectroscopy. Various concentrations of the sulfonic acid group can be introduced into the polysulfone without degrading its physical strength. The resulting SPSF shows enhanced hydrophilicity and electrochemical properties for use as an ion-exchange membrane. Studies with CV indicate that the anodic and cathodic current peaks are symmetrically shaped irrespective of the scan rate over the range 50 to 500 mV s⁻¹ and the mobility of sodium ions in the SPSF membrane matrix is high.

Diffusion coefficients are obtained by curve fitting to experimental results and increase from 1.136×10^{-11} to 1.082×10^{-12} cm² s⁻¹ as the sulfonic acid group concentration is increased from 0.672 to 1.18 mmol/g membrane in 0.5 M NaCl electrolyte at open-circuit. The double-layer capacitance is found to depend on sulfonic acid group concentration, electrolyte concentration, and reduction potential, but not on membrane thickness. The total resistance depends on sulfonic acid group concentration, electrolyte concentration, membrane thickness, and reduction potential.

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