Novel composite proton-exchange membrane based on silica-anchored sulfonic acid (SASA)

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Abstract

A new approach to the synthesis of a low-cost proton-exchange composite membrane (C-PEM) based on PVDF and silica with surface-anchored sulfonic acid (SASA) groups, is presented for the first time. SASA membranes of different compositions have been prepared and characterized with the use of SEM, DSC, TGA, BET and electrochemical techniques. The room-temperature conductivity of SASA-based C-PEMs, is in the range of 2.0–50 mS cm^{-1}. The equivalent weight of two SASA powders, SASA3(A) and SASA4(A) are 1600 and 2500 g equiv.$^{-1}$ respectively. The typical pore size as measured by BET is about 4 nm. The membrane is thermally stable up to 250 °C. Direct methanol fuel cells (DMFCs) have been assembled with some of the membranes. Preliminary tests show that the cell resistance with a non-optimized membrane is in the range of 3 Ω cm^{-2}, therefore the maximum cell power density achieved so far does not exceed 32 mW cm^{-2} at 70 °C. The crossover-current density for a 100 μm-thick membrane DMFC measured in 1 M methanol at 80 °C is 110 mA cm^{-2}.
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1. Introduction

Because of their high efficiency, simplicity and low working temperatures, direct methanol fuel cells (DMFCs) employing polymer electrolyte membranes are among the most attractive power sources for a variety of mobile and stationary applications, including small electric vehicles [1–7]. In such cells the methanol is fed directly into the anode compartment or a mixing chamber without reforming. Proton-conducting membranes are key elements of polymer-electrolyte-membrane fuel cells (PEMFCs) [4–7] in general and, particularly, in DMFCs. Nafion (DuPont) is the most commonly used membrane in fuel cells operating at near-ambient temperatures (up to 80 °C). In DMFC applications, Nafion has three major disadvantages: very high cost, ($780 m^{-2} [8] or about $3000 kg^{-1}), marked dependence of the conductivity on its water content and very high methanol crossover. For Nafion 117, the crossover is 125–150

and 250–300 mA cm^{-2} for 1 M methanol at 60 and 90 °C, respectively [9,10]. Methanol, crossing over from the anode side through the Nafion membrane to the cathode side, reacts with oxygen, produces heat, and reduces the energy-conversion efficiency. In recent years there has been an intensive effort to develop a low-cost membrane to replace Nafion, with significant progress being made [7,11,12]. Various membranes, such as sulfonated polysulfones, sulfonated polyetherketones, and sulfonated polyetheretherketones, with basic polymers such as poly(4-vinylpyridine), polybenzimidazole, or substituted polysulfones have been synthesized in attempts to develop a suitable DMFC membrane [13]. However, the sulfonation of these polymers leads to the formation of water-soluble polymers at high sulfonation levels. Numerous proton-conducting membranes have been reviewed [7].

We recently reported the development of a new nanoporous proton-conducting membrane (NP-PCM) and have applied it in a DMFC and in a direct ethylene glycol fuel cell (DEGFC) [12,14–17]. This membrane consists of PVDF as a binder, nano-size silica powder and an acid. The use of the NP-PCM in the DMFC offers several advantages over the Nafion-based DMFC:

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more than two orders of magnitude lower membrane cost, pores one-half to one-third the size and up to an order of magnitude lower methanol crossover.

With the aim of developing a low-cost, high-temperature membrane, we have synthesized and characterized novel composite proton-exchange membranes (C-PEMs). Preliminary results were recently published [18,19]. These membranes consist of a polymer binder (PVDF) and nanosize powders of silica with surface-anchored sulfonic acid groups (unlike Nafion, where the sulfonic groups are attached to the polymer backbone). The nanosize silica particles function as water retainers in the membrane at elevated temperatures.

2. Experimental

The SASA membranes were prepared by two different routes. The first, (A), involved the casting of a C-PEM from a suspension of a previously synthesized nanosize SASA powder and PVDF (Kynar 2801, EIF Atochem) in cyclopentanone. The SASA powder was prepared by the silanization of nanosize silica particles followed by sulfonation. This resulted in sulfonated nanosize silica particles. The silanization reagents were diphenyldichlorosilane (DPDClS) or 3-mercaptopropyltrimethoxysilane (MPTMS), both in xylene. The sulfonation reagents were chlorosulfonic acid (in the case of silanization with DPDClS) and O_3 (in the case of silanization with MPTMS), both in chloroform. The oxidation step of the latter involves the conversion of the –SH group originally in MPTMS to $-SO_3H$.

The second procedure (B) involved the casting of a film directly from a cyclopentanone suspension containing the silanes, the silica nanosize powder and the PVDF binder polymer. The silanization reagents here were tetraethoxysilane (TEOS) and MPTMS. The sulfonation reagents were 50% H_2O_2, H_2SO_4 and NaF. In an aqueous solution, the silanes' –OR groups undergo hydrolysis and condensation. NaF functions as a catalyst.

Various membrane compositions and types of SASA powders were tested. The conductivity of SASA membranes was measured at room temperature (under atmospheric pressure while keeping the membrane wet during the measurement), after membrane activation pretreatment. As common for PEM membranes it involved immersion in 3 M H_2SO_4 at 70 °C for 1 h (to remove possibly surface-adsorbed impurities) with two subsequent water washings (to remove acid traces and to allow water absorption for the achievement of maximal conductivity), each for 1 h at 90 °C. All membranes were pretreated before conductivity measurements.

SASA powders were back-titrated in order to determine their equivalent weight (EW = g polymer mol^{-1} SO$_3$H sites). Samples were immersed in 1 M H_2SO_4 solution at 70 °C for 1 h and then in water (under the same conditions). Repeated rinsing was carried out until a constant pH value was achieved. Samples were vacuum dried at 60 °C for 12 h and then immersed in 0.01 M NaOH solution for 24 h in a sealed flask. The NaOH solution was titrated with 0.01 M HCl solution using the bromocresol green indicator. The pore-size distribution of dry membranes

was tested with the use of a Quantachrome NOVA 2200 surface area analyzer and calculated by the DFT (density functional theory) method. SEM micrographs were taken with the use of a JEOL JSM-3600 scanning electron microscope.

The TGA tests were carried out with a TA Instruments model SDT 2960. TGA-DTA runs were recorded at a scan rate of 10° min^{-1} up to 300 °C. The sample compartment was flushed with dried, UHP argon at all times. For the DSC tests the samples were sealed in alodined (covered by high resistant and compact surface oxide film) aluminum DSC pans. The DSC tests were conducted with a TA Instruments model 2100 at a scan rate of 10° min^{-1} from RT to 300 °C in an argon atmosphere.

A 7 cm^2-area fuel cell was built with a single-side Elat (E-TEK) cathode, 4.0 mg cm^{-2} Pt-black loading, 0.6–0.8 mg cm^{-2} Nafion loading, and a home-made anode consisting of Pt–Ru 1:1 HiSPec 6000, JM (2.0 mg cm^{-2} Pt loading), spread on plain TGPH-60 (E-TEK) Toray carbon paper 0.17 mm thick. The MEA was hot-pressed at 100 °C under a pressure of 24 kg cm^{-2} (the membrane itself was pretreated, as specified earlier, before MEA formation). Dry oxygen was fed into the cathode compartment at 3 atm and at a rate of 45 mL min^{-1}. An aqueous solution of 1 M methanol was circulated towards the anode with the use of a peristaltic pump (Masterflex L/S Cole-Parmer Instrument Co.) at a flow rate of 5 mL min^{-1}.

3. Results and discussion

A silica-anchored sulfonic acid (SASA) particle is schematically presented in Fig. 1. It is obvious that the conductivity of a membrane depends on its equivalent weight (EW = g polymer mol^{-1} SO$_3$H sites). Since the membrane is based on SASA powder, its EW depends on that of the powder (g powder mol^{-1} SO$_3$H sites). A decrease in EW would lead to an increase in conductivity. The calculated minimal value for the EW of a pure silica powder is based on the manufacturer's value [20] of 2.5 silanol groups nm^{-2}. Assuming a complete reaction (where the number of acid groups is equal to that of the silanol groups), EW was calculated to be 600–1600 g equiv.$^{-1}$ for surface areas of 400–150 m^2 g^{-1}, respectively. If it is taken into account that the membrane also contains PVDF, the effective EW of the membrane should be somewhat higher. Such low EW values,
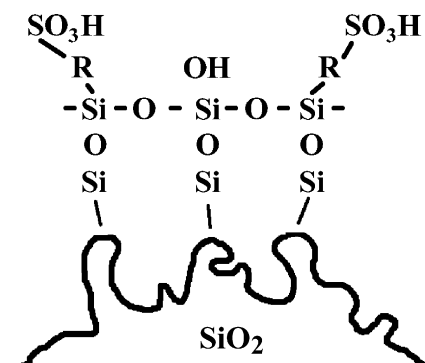

Fig. 1. Schematic representation of surface-anchored sulfonic acid groups attached to the silica particles.

Table 1
Compositions of the different SASA membranes

Membrane code (route A/B)	SASA powder[a]	SASA powder (V%)[b]	PVDF (V%)[b]	Pure silica (V%)[b]	Functional group
S1(A)	SASA 1(A)	16	24	–	
S2(A)	SASA 2(A)	10	10	–	
S3(A)	SASA 3(A)	18	21	–	
S4(A)	SASA 4(A)	12	28	–	$-Si-Ph-SO_3H$
S5(A)	SASA 5 (A)	12	28	–	
S6(A)	SASA 1(A)	9	12	3	
[c]S1(B)		–	28	12	
[c]S2(B)		–	40	0	$-Si-(CH_2)_3-SO_3H$

[a] Each SASA powder was prepared from different silica powder.

[b] The rest is void volume.

[c] The preparation procedure involved silanes (MPTMS, TEOS) condensation via sol–gel process and formation of sulfonated silica, together with PVDF, according to route B, specified in the experimental section.

which are similar to the literature data [7], indicate considerable promise of the SASA membrane concept.

In order to allow sequential contact between the adjacent sulfonic acid groups, an important structural requirement must be fulfilled: the polymer binder supporting the SASA powder must not cover it completely (Fig. 2). The gap between two adjacent SASA particles must be as small as possible in order to allow continuous and fast transport of protons. In this paper we present preliminary results on a narrow range of SASA compositions. In an attempt to understand the complex interplay between composition and properties with the final goal of developing a highly conductive membrane, a variety of SASA membranes were prepared (Table 1). SEM images reveal that the use of different components and procedures causes changes in membrane morphology, as can be seen in Figs. 3 and 4. SASA membranes prepared by route A (casting of previously synthesized SASA powder and PVDF binder) are denser and free of
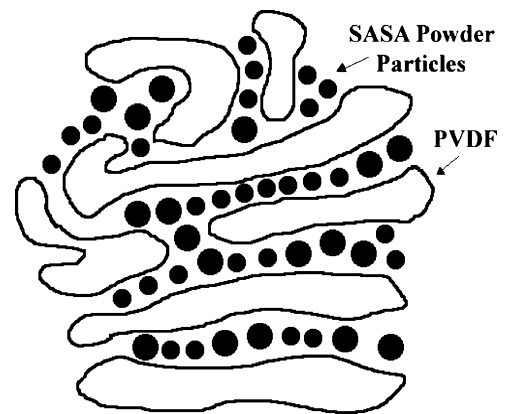

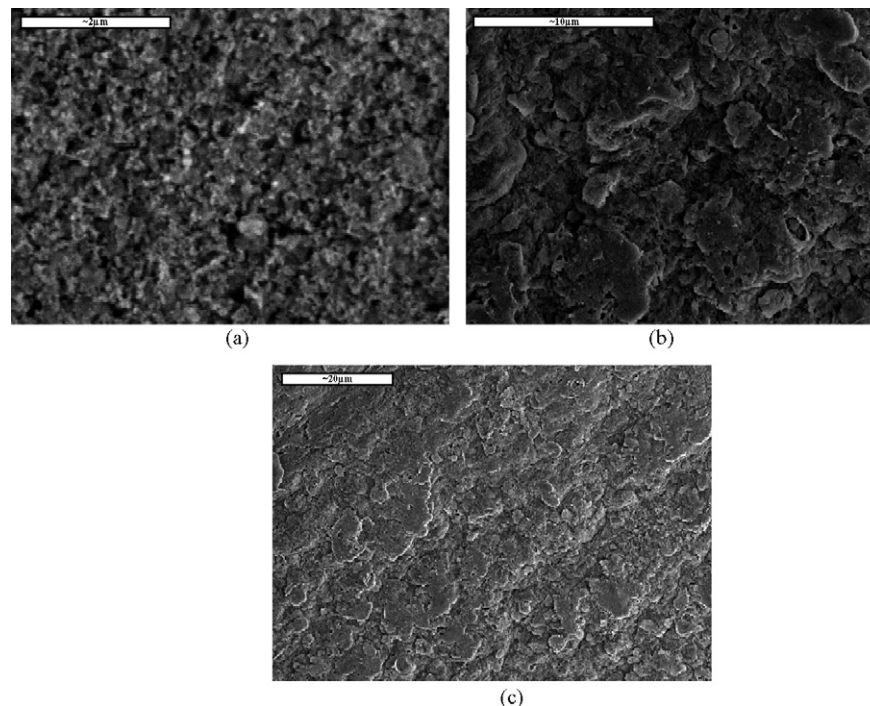
Fig. 2. SASA membrane desired model.

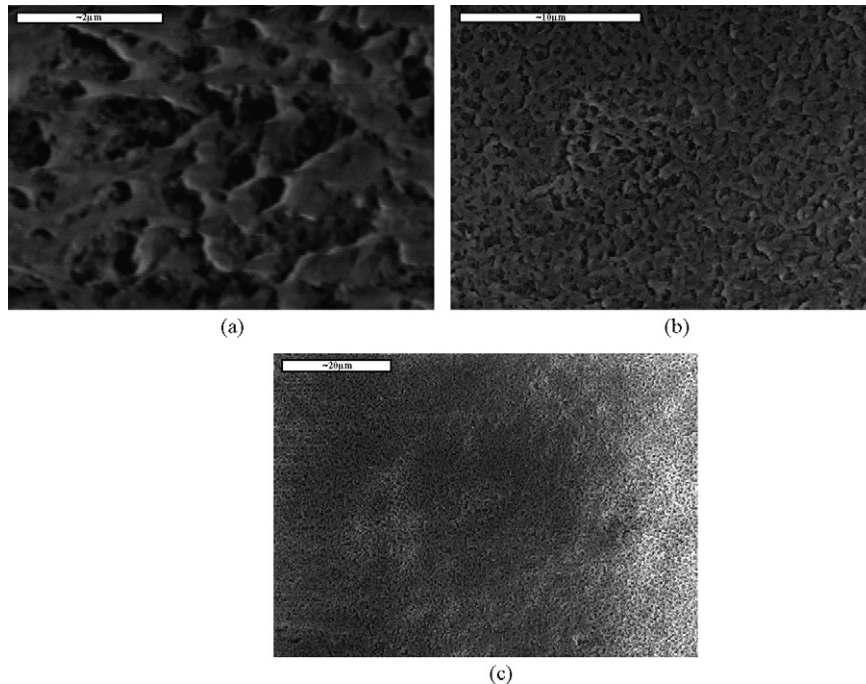Fig. 3. Typical SEM micrographs of a type A C-PEM., magnifications: (a) 20,000×; (b) 5000×; (c) 1500×.

Fig. 4. Typical SEM micrograph of a type B C-PEM., magnifications: (a) 20,000×; (b) 5000×; (c) 1500×.

holes or cracks larger than 0.3 μm (Fig. 3). SASA membranes prepared by route B are smoother, less dense, more porous and free of holes or cracks larger than 1 μm (Fig. 4). The pore-size distribution (PSD) calculated by the DFT method shows that for the dry type A membranes, the dominant pore size is 4 nm (Fig. 5). For comparison, Nafion has a wide spectrum of pore sizes ranging from 1 to 100 nm with an average value of about 2 nm [17] to 4 nm [7].

Back titrations of some of the SASA powders were performed and the equivalent weights of these powders were calculated. The EWs of two SASA powders, SASA3(A) and SASA4(A) are 1600 and 2500 g equiv.$^{-1}$ respectively, a bit higher than the minimal calculated values of 600–1600 g equiv.$^{-1}$ For comparison, a film of Nafion 117 was also back-titrated using

this method. The EW calculated was 940 g equiv.$^{-1}$ This indicates that the "real" EW values of our SASA membranes are a bit higher than those measured here. These seem to be the maximum values, as it is quite difficult to titrate a "solid" acid. It may also indicate that either the silanization or sulfonation process, or both, were not complete and not every silanol group is associated with an acid group. Membrane conductivities were measured *ex situ* at room temperature before and after a hot-press process (Table 2) and *in situ* at 50–100 °C (Table 3). The relatively low proton conductivities of these membranes
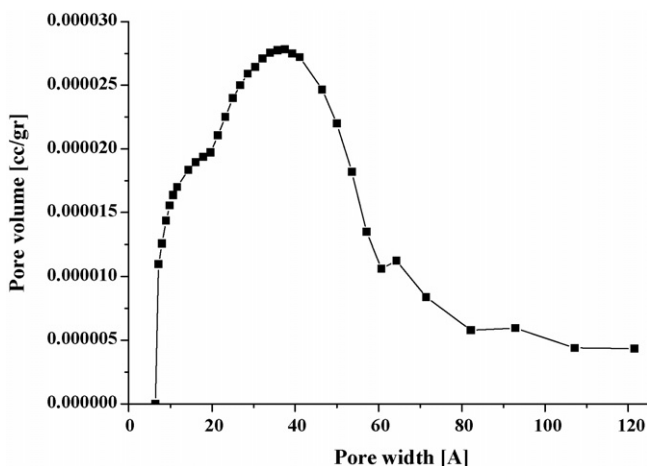

Fig. 5. Pore-size distribution (DFT method) for dry S1(A) C-PEM.

Table 2
Hot-press influence on SASA membrane conductivity (*ex situ*)

Membrane code	Hot-press conditions at $T = 100\,^{\circ}\mathrm{C}$		Thickness (μm)	Conductivity (mS cm^{-1})
	Pressure (kg cm^{-2})	Time (s)		
S1(A)	–	–	70	12
	24	60	91	50
S2(A)	–	–	90	14
	24	60	50	24
S3(A)	–	–	95	30
	24/86	60/180	71	3
S4(A)	24	60	225	4
S5(A)	–	–	43	20
	24	60	55	2
S6(A)	–	–	–	5
S1(B)	–	–	72	20
	24	60	50	1.1
S2(B)	–	–	90	52

Table 3
In situ measurements

Membrane code (type)	Temperature (°C)	Cell resistance (Ω)	Membrane conductivity (mS cm^{-1})
	39	0.57	2.0
S2(A)	60	0.46	2.5
	94	0.31	3.6
	50	0.43	3.3
	55	0.41	3.5
	60	0.40	3.6
S6(A)	75	0.40	3.6
	83	0.41	3.5
	90	0.40	3.6
	100	0.39	3.7

points to the fact that the formation of surface groups falls short of the required amount and that too big gap exists between adjacent SASA particles. Further work is needed to improve these processes.

The hot-press procedure is an essential step in MEA fabrication and therefore its influence on conductivity is of particular concern in MEA and DMFC engineering. Table 2 summarizes the room-temperature conductivities of several types of A and B membranes both before and after hot-pressing (measured on two to three different samples of each membrane). Up to now, we have not found any clear correlation among the synthesis procedure, the hot-press effect and the conductivity. As can be seen from the table, two types of membrane prepared by route A (S1(A) and S2(A)) showed an increase in conductivity by a factor two to four after hot pressing, probably due to improved contacts between the SASA nano particles. However, several other membranes (S3(A), S5(A) and S1(B)) showed a decrease in conductivity after hot pressing. We attribute this to possible structure collapse.

Some results of the thermal analysis of the powders and membranes are shown in Figs. 6–8. All SASA powders were found to be stable up to 350 °C (Fig. 6). The roughly 2.5% weight loss
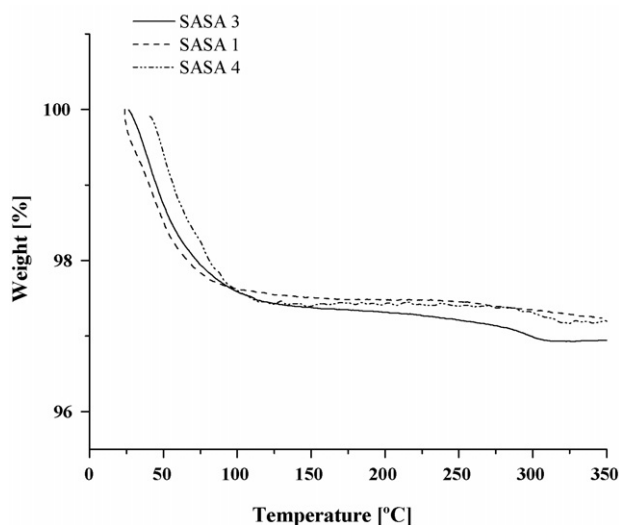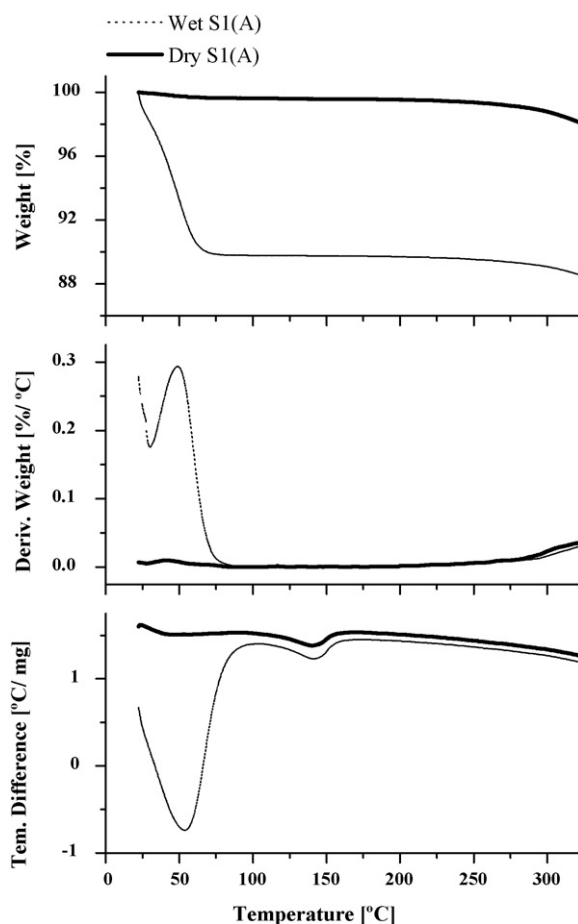

Fig. 7. TGA-DTA curves of dry and wet S1(A) C-PEM.

at the beginning of the heating run is assigned to the release of surface water. Figs. 7 and 8 show the results of TGA-DTA and DSC tests for dry and wet S1(A). As in the case of powder, there is an endothermic 0.4% weight loss (WL) at about 42 °C on heating of the dry membrane and 12% WL of the wet

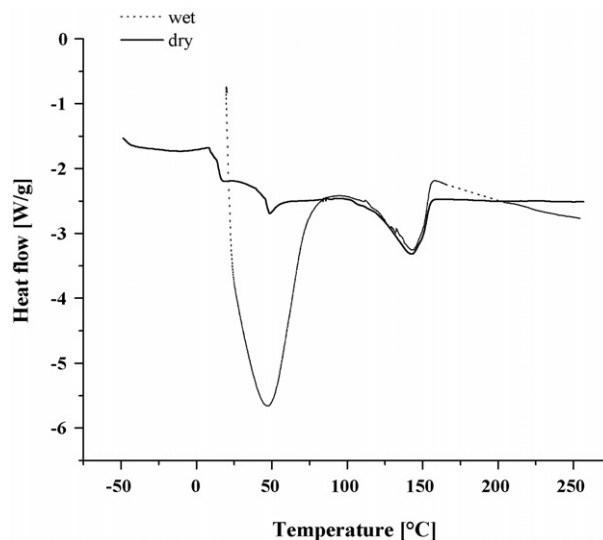Fig. 6. TGA traces of SASA 1(A), 3(A), 4(A) powders.

Fig. 8. DSC runs of dry and wet S1(A) C-PEM.

one. It will be noted that the low-temperature WL is smaller in the dry membrane than it is in the pristine SASA1(A) powder. This can be explained by the lower content of silica in the membrane due to the presence of PVDF. In the wet sample, the water desorption seems to be a two-stage process as shown in the DTG curve, where a strong shoulder and peak are seen between 25 and 100 °C. These may be related to the existence of two energetically different surface sites. At 140 °C there is a phase transition appearing both in the dry and wet membrane, which is not accompanied by a WL. This endotherm is associated with the melting of the PVDF. The glass transition temperature of the 12%(v/v) SASA1(A), 44%(v/v) PVDF membrane was 14.8 °C, indicating that incorporation of ceramic powder shifts the Tg of the polymer toward higher temperatures.

Similar TGA and DSC tests were run with other membranes and all the PVDF-SASA membranes were found to be stable up to 250 °C.

Several 7 cm^2-area DMFCs with different membranes (~100 μm thick) were constructed and operated at ~40–100 °C with dry oxygen. Membrane conductivity, calculated from the cell resistance, increases with temperature from 2.0 to 3.6 mS cm^{-1} and from 3.3 to 3.7 mS cm^{-1} for the S2(A) and S6(A) samples, respectively (Table 3). The OCV value of the cell at 70 °C (Fig. 9) was 0.66 V, somewhat lower than that of a Nafion-based DMFC. This typically indicates poor cathode performance, which may be caused by imperfect interfacial contact followed by too-large cathode-to-membrane resistance. Up to now, the best cell has reached a maximum current of 140 mA cm^{-2} at about 0.2 V. The cell power is 32 mW cm^{-2} (Fig. 9). The *V/I* curve is linear, typical of a cell with high internal resistance. The ohmic voltage drop is high: 420 mV at 0.14 A cm^{-2}. As suggested above, the major reasons for the low power are high membrane resistance and probably poor interfacial (electrode-to-membrane) contact. Methanol crossover in 1 M methanol and at 80 °C for a 100 μm-thick membrane cell was 110 mA cm^{-2}, similar to that of a Nafion-based DMFC. While the DMFC power achieved so far is not at the state-of-the-art level, there appears to be little doubt of the importance of a new concept of PEM with silica-surface-anchored sulfonic groups. Work is in progress on optimization of SASA membranes and their application in both DMFC and hydrogen fuel cells.

4. Summary

A novel composite PEM based on silica-anchored sulfonic acid (SASA) powder and a polymer binder was synthesized and characterized for the first time. Two different synthesis routes were used. Membranes prepared by route A were denser and free of holes or cracks larger than 0.3 μm, while membranes prepared by route B were smoother, less dense, more porous and free of holes or cracks larger than 1 μm. PSD measurements revealed that a typical pore in the membrane had a diameter of 4 nm. The membranes were stable up to 250 °C. The estimated maximum values for the EWs of the SASA powders were in the range of 1600 to 2500 g equiv.$^{-1}$, a bit higher than the minimal theoretical value of 600–1600 g equiv.$^{-1}$, calculated for pure silica powders. This is the main reason for the relatively low membrane conductivity (2–50 mS cm^{-1}). DMFCs with SASA-based membranes showed a maximum power density of 32 mW cm^{-2} at 70 °C and a typical *V/I* curve for a cell with high internal resistance. There is need for further research on the optimization of membranes properties.

References

[1] X. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996).
[2] N.A. Hampson, M.J. Wilars, B.D. McNicol, J. Power Sources 4 (1979) 191.
[3] Kim Dae Sik, Park Ho Bum, Rhim Ji Won, Lee Young Moo, J. Membr. Sci. 240 (1–2) (2004) 37–48.
[4] J.A. Kerres, J. Membr. Sci. 185 (2001) 3.
[5] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29.
[6] L. Carrette, K.A. Friedrich, U. Stimming, Chemphyschem 1 (2000) 162.
[7] B. Smitha, S. Sridhar, A.A. Khan, J. Membr. Sci. 259 (2005) 10.
[8] S.R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M. Smart, S. Surampudi, G. Halpert, Proton Conducting Fuel Cells I, in: S. Gottesfeld, G. Halpert, A. Langrebe, (Eds.), PV 95-23, The Electrochemical Society Proceedings Series, Pennington, NJ, 1995, p. 261.
[9] S.R. Narayanan, W. Chun, T.I. Valdez, B. Jeffries-Nakamura, H. Frank, S. Surumpudi, G. Halpert, J. Kosek, C. Cropley, A.B. La Conti, M. Smart, Q.J. Wang, G.S. Prakash, G. Olah, Recent Advances in High-Performance Direct Methanol Fuel Cells, NASA JPL, 1996, web site: http://techreports.jpl.nasa.gov/jpltrs.cgi?fuel+cell.
[10] S.J. Warthesen, D.A. Shores, Proceedings of the Extended Abstracts of the 3rd International Symposium on New Materials for Electrochemical Systems, Montreal, Canada, July 4–8, 1999, p. 69.
[11] F.N. Cornet, G. Geble, R. Mercier, M. Pineri, B. Sillion, in: O. Savadogo, P.R. Roberge (Eds.), New Materials for Fuel Cell and Modern Battery Systems II, Ecole Polytechnique Montreal, Montreal, 1997, p. 818.
[12] E. Peled, T. Duvdevani, A. Melman, Electrochem. Solid-State Lett. 1 (1998) 210.
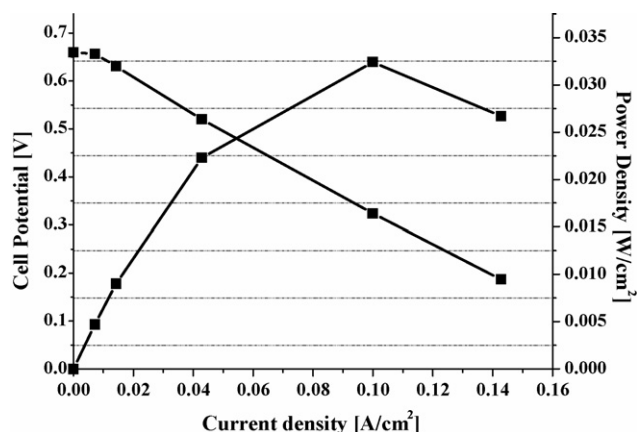[13] J. Kerres, A. Ullrich, F. Meier, T. Haring, Solid State Ionics 125 (1999) 243.

Fig. 9. Performance of S1(A)-based DMFC, 70 °C, 3 atm. O$_2$ at 45 mL min^{-1}, 1 M MeOH at 5 mL min^{-1}.

[14] E. Peled, T. Duvdevani, A. Aharon, A. Melman, Electrochem. Solid-State Lett. 3 (2000) 525.

[15] E. Peled, T. Duvdevani, A. Aharon, A. Melman, Electrochem. Solid-State Lett. 4 (4) (2001) A38–A41.

[16] E. Peled, Battery 2005 Paris, Euroforum France, Speakers Documentation, June (2005). www.batteriescongress.com.

[17] E. Peled, V. Livshits, T. Duvdevani, J. Power Sources 106 (2002) 245–248.

[18] US Patent 6447943.

[19] E. Peled, T. Duvdevani, M. Philosoph, ISPE-9 Proceedings, Mragowo-Poland, 2004.

[20] M. Gunther, F. Horst, Technical bulletin pigments, Number 11, 1993.