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Development of Solid-State Alkaline Electrolytes for Solid Alkaline Fuel Cells

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Summary: Solid-state alkaline electrolytes were prepared from chloromethylated polysuflone (CMPSf) and a number of mono- and diamine compounds for solid alkaline fuel cell (SAFC) applications. Chloromethyl-groups as substituents for aromatic nuclei were introduced to an aromatic polymer in the presence of a Friedel-Crafts catalyst and then the basic groups into polymer by amination using *N*-trimethylamine (TMA) and *N*,*N*,*N*′,*N*′-tetraemethylhexanediamine (TMHDA). The properties of the solid-state alkaline electrolytes were invetigated in terms of OH^- conductivity, water content and thermal stability.

Keywords: amination; solid alkaline fuel cell; solid-state alkaline electrolyte

Introduction

Alkaline fuel cells (AFCs) are hydrogen-fuelled cells with a liquid electrolyte such as KOH(*aq*) and are the best performing of all known fuel cells operable below 200 °C. This is mainly due to the facile kinetics at the cathode as well as at anode (Equation (1)–(3)); cheaper non-noble metal catalyst can be used such as nickel and silver.[1,2]

$$\text{Anode}\quad H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad E_o = -0.83V \tag{1}$$

$$\text{Cathode}\quad 1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad E_o = 0.40V \tag{2}$$

$$\text{Overall}\quad H_2 + 1/2O_2 \rightarrow H_2O \quad E_o = 1.23V \tag{3}$$

However, the electrolyte and electrode degradation caused by the formation of carbonate/bicarbonate (CO_3^{2-}/HCO_3^-) in the liquid alkaline electrolyte on reaction of OH^- ions with CO_2 contamination in the oxidant gas stream has limited the application such as NASA's space shuttle orbiter. Such a problem can be solved by using solid-state alkaline electrolytes.[2–4] They allow for increasing the volumetric energy density, avoiding problems of leakage and preventing the gas electrode flooding mainly responsible for the death of the fuel cells using polymeric electrolytes (*i.e.*, PEMFC, DMFC). Thus cheap solid-state alkaline electrolytes with good electrochemical and chemical stability with time would be interesting for solid alkaline fuel cells.

In this study a particular interest was devoted to preparation of the solid-state alkaline electrolytes. The electrolytes were based on chloromethylated polysulfone (CMPSf). For conducting hydroxide ions the basic anion-exchangeable groups were introduced into polymer by amination using i) monoamine, ii) diamine and iii) mixture of mono- and diamine. This study was investigated to improve electrochemical properties and thermal stability of solid-state alkaline electrolytes and then the electrolytes were used for fabricating membrane-electrode assemblies (MEAs) for SAFC operations.

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Experimental Part

Chloromethylation

Chloromethylation of PSf (Udel® P-1700, Solvay Advanced Polymers, L.L.C, USA) was carried out in a four-neck round-bottom flask fitted with a mechanical stirrer. The PSf was dissolved in 1,1,2,2-tetrachloroethane (TCE, Sigma-Aldrich) to make a 12 wt.% solution. Chloromethylmethylether (CMME, Sigma-Aldrich) (PSf:CMME = 1:4 in mole) was added in the presence of $ZnCl_2$ (Junsei Chemical, Japan) as catalyst. The solution was transferred to the reaction flask and heated in an oil bath to 40 °C and then was stirred for 1.5–6 h under a N_2 atmosphere. The CMPSfs (Figure 1) were precipitated in methanol, washed in deionized water for 24 h, filtered and then dried in a vacuum oven for 24 h at 80 °C.

Amination

Dried CMPSfs were dissolved in DMF, DMAc, NMP and DMSO to be 11 wt% solutions. Experimental conditions for amination of CMPSf by monoamine, diamine and mono-/diamine mixture are summarized in Table 1.

The amination reagents were added in the solutions. The solutions were transferred to the reaction flask and heated in an oil bath to 30 °C and then was stirred for 0.5–200 h under a N_2 atmosphere. The resulting solutions were precipitated in methanol, washed in deionized water for 24 h, filtered and then dried in a vacuum oven for 24 h at 80 °C. Dry aminated CMPSfs were dissolved in DMF, DMAc, NMP and DMSO to be 11 wt% solutions. The resulting solutions were degassed under vacuum and cast onto a flat-bottom Petri dish for membrane formation. The membranes were dried in an oven at 80 °C for 12 h and then under vacuum at 100 °C for 1 day. Dry membranes were peeled off from the substrate with deionized water. Thickness of all the membranes was 40–50 μm. The membranes were stored in 0.5 M KOH solution for 1 day prior to their use.

The solid-state alkaline electrolytes are typically prepared by amination of halomethylated polymers with monoamines such as TMA as shown in Figure 2. In this study the diamine (*i.e.*, TMHDA) used for introduction of the basic groups into polymer. The quaternization with diamines

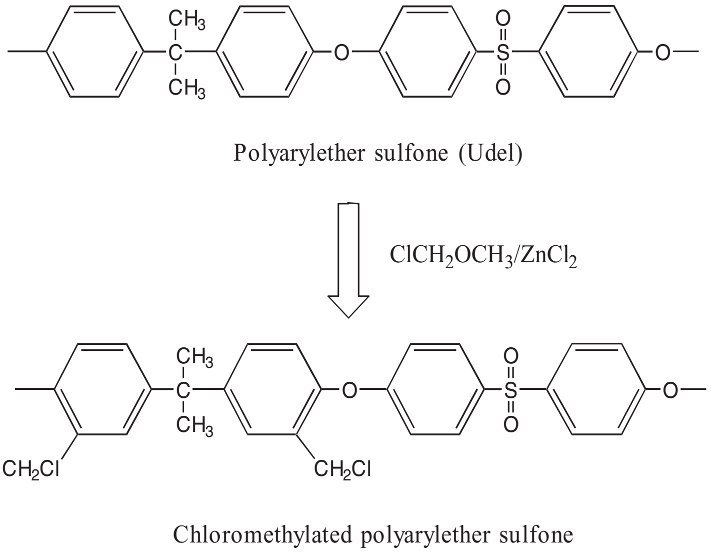

Figure 1.
Scheme of chloromethylation of PSfs by CMME.

Table 1.
Experimental condition for amination of CMPSf.

Amination type	Reagent*	Amination time (h)	Amination temp. (°C)
Monoamine	TMA	10–200	30
Diamine	TMHDA**	0.5	30
Mixture	TMA/TMHDA	10–200	30

* CMPSf : reagent = 1:4 in mole; All reagents were supplied by Sigma-Aldrich;
** *N*,*N*,*N*′,*N*′-tetramethylhexane methylenediamine.

proceeds as a mono-reactions (mono-quaternization) and as a cross-linking reaction (bi-quaternization) (Figure 3).

Characterization of the Solid-State Alkaline Electrolytes

The OH^- conductivity of the membranes was measured by an AC impedance spectroscopy using a Solarton 1260 frequency response analyzer interfaced to an EG&G 270 multistat. The measurement was carried out in the potentiostatic mode over the frequency range from 1 Hz to 1 MHz with oscillating voltage of 5 mV. The laboratory-made four-probe conductivity cell configuration is similar to that reported in the literature.[5] The cell was kept in a temperature- and relative humidity-controlled sealed off vessel (25 °C and 100% RH). The conductivity of the samples was calculated by the Equation (4):

$$\sigma = \frac{d}{RS} \tag{4}$$

where σ is the OH^- conductivity, d the membrane thickness, R the membrane resistance derived from the impedance value at zero phase angle and S the membrane area.

Water content (WC) of the membranes was determined from the difference in weight before and after hydration. Membrane samples were dried at 110 °C under vacuum (W_{dry}). The samples were then immersed in deionized water for 1 day at the given temperature (*i.e.*, 25 °C), removed from water, surface attached water was wiped out with filter paper and immediately weighed (W_{wet}). WC was reported as absorbed water weight percent with respect to dry membranes (WC % = $(W_{wet} - W_{dry})/W_{dry}{}^{*}100$):

Thermogravimetric analysis (TGA) was carried out on TGA 2050 instrument from TA instruments, USA. Initially the samples were heated under nitrogen atmosphere up to 150 °C, cooled down to 80 °C to remove moisture of the samples and reheated untill 400 °C at the rate of 10 °C/min under nitrogen atmosphere.

MEA Fabrication and SAFC Operations

Pt/C (40 wt%, Johnson & Matthey, USA) was employed as catalyst. The platinum loading for both anode and cathode was 0.5 mg cm^{-2}. The catalyst slurries were prepared by mixing the catalyst powder and ionomer solution (5 wt.%, laboratory-made) in the organic solvent which is the same for casting. The slurries were then sonicated for 1 h and were kept being mixed

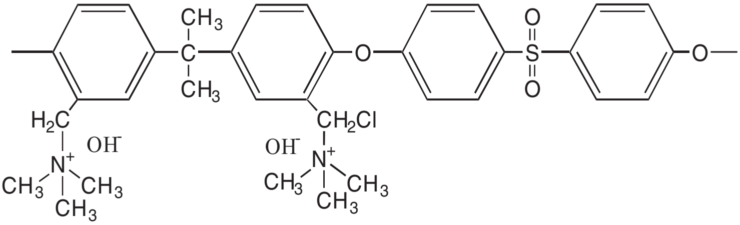

Figure 2.
Amination of CMPSfs by monoamine (TMA).

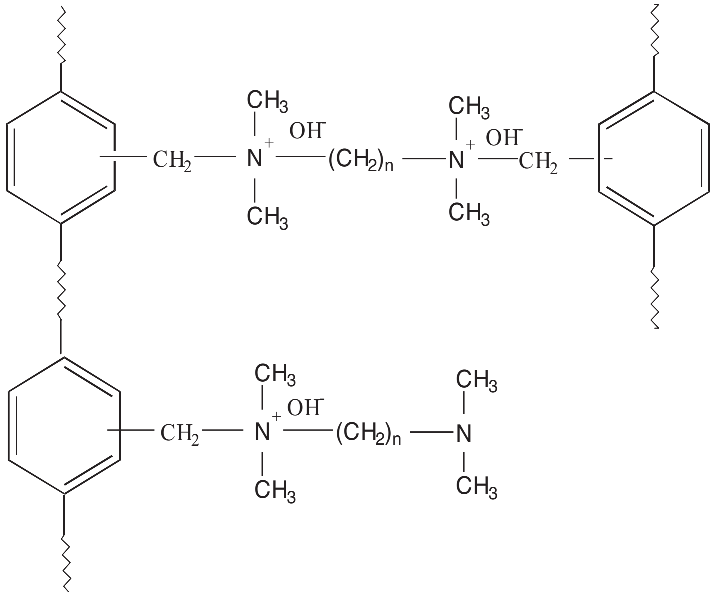

Figure 3.
Amination of CMPSfs by diamine (in case of TMHDA, n = 6).

on a stirrer for 3 days. Each catalyst slurry was applied to PTFE-impregnated Toray 250 carbon paper (waterproof by 8 wt.% PTFE) by a spraying method. The carbon papers were dried in the oven at 100 °C to determine the amount of catalyst loading. The carbon papers sandwiched the membranes. The details on MEA fabrication and SAFC operations are summarized in Table 2.

Results and Discussion

Optimization of Chloromethylation Time

Chloromethylation was optimized in terms of reaction time. The optimal chloromethylation time was determined by comparing OH$^-$ conducitivity of solid-state alkaline electrolytes under the same amination condition that is the amination temperature of 30 °C, the amination time of 24 h and the weight ratio of CMPSf to TMA of 1:4 and the same casting condition. Figure 4 shows the change in the OH$^-$ conductivity and water content as a function of chloromethylation time under the fixed amination condition. The OH$^-$ conductivity increases as chloromethylation time increases up to 3.5 h and then abruptly decreases as chloromethylation time increases. The abrupt decrease in OH$^-$ conductivity is mainly due to self-cross-linking property of PSf. The water

Table 2.
Experimental condition for MEA fabrication and SAFC operation.

SAFC	Anode	Cathode	Remark
Catalyst	Pt/C	Pt/C	Johnson & Matthey 40 wt.%
Ionomber binder	two type	two type	5 wt.% in DMAc
Loading amount (mg cm^{-2})	0.5	0.5	catalyst weight basis
Active area (cm^2)	10	10	
Fuel/Oxidant	H_2	Air	humidified at 55 °C
Utilization (%)	70	40	
Cell temperature (°C)	60	60	

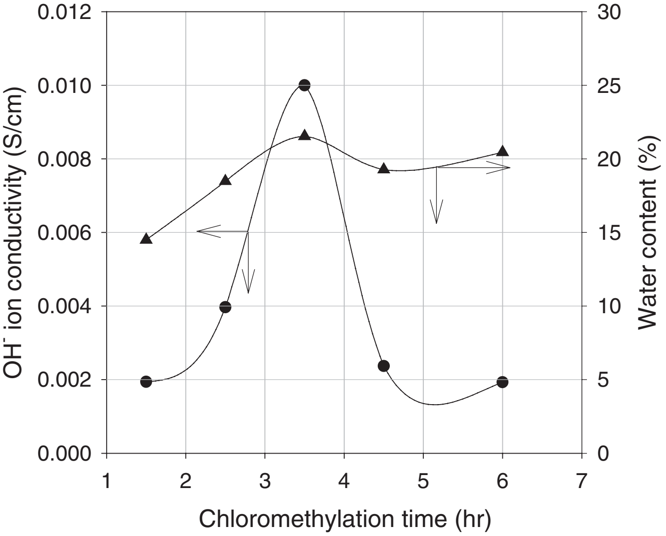

Figure 4.
Variation of OH⁻ conductivity and water content as a function of chloromethlyation time (Fixed condition - i) the amination condition: temperature, 30 °C; time, 24 h; the weight ratio of CMPSf to TMA, 1:4 ii) the casting condition: solvent, DMAc).

content shows a typical trend with OH⁻ conductivity, which is that water content is proportional to ionic conductivity. As a result the chloromethylation time is afterward fixed to be 3.5 h.

Optimization of Amination Time

Amination were optimized in terms of reaction time. The optimal amination time was determined by comparing OH⁻ conducitivity of solid-state alkaline electrolytes under the same chloromethylation condition that is the amination temperature of 40 °C, the amination time of 3.5 h and the weight ratio of PSf to CMME of 1:4 and the same casting condition. Figure 5 shows the change in the OH⁻ conductivity and water content as a function of amination time under the fixed chloromethylation condition. The OH⁻ conductivity increases up to 100 h and then slowly decreases as amination time increases. It is noted that the amination above 48 h does not increase OH⁻ conductivity much. For the effieiciency of reaction time the amination time was fixed to be 48 h for all further preparation of solid-alkaline electrolytes.

Optimization of Amination Reagent

For optimization of amination processes CMPSfs were aminated at various ratios of TMA to TMHDA (*i.e.*, 1:0, 0:1, 1:1, 1:2, 2:1, 3:1 and 1:3). The electrolyte aminated by the diamine (in case of the ratio of 0:1) showed very good OH⁻ conductivity, but bad thermal stability due to short amination time (90 sec) as shown in Figure 6. No longer amination than 90 sec was allowed due to fast cross-linking and gelation of CMPSf. Other amination conditions with high proportion of the diamine in mixtures led to a successive reaction during the optimized amination time (*i.e*, 48 h in this study), but bi-quarternization of the diamine in mixtures caused high cross-linking of PSf to decrease OH⁻ conductivity. It is inferred that appropriate content of the diamine in mixtures enables to give optimal cross-linking to improve thermal stability by bi-quaterization of TMHDA as well as to give additional ion-exchangeable site for OH⁻ to improve conductivity by mono-quaternization of TMHDA (see Figure 2 and 3). In fact, the solid-state alkaline electrolyte aminated by the TMA/

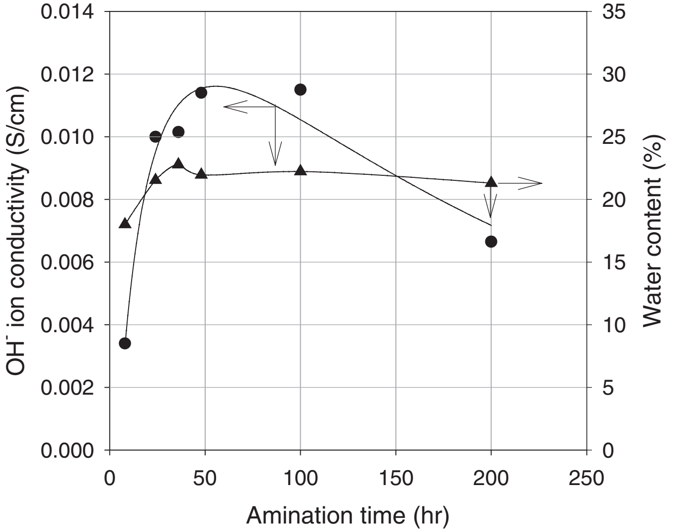

Figure 5.
Variation of OH^- conductivity and water content as a function of amination time (Fixed condition - i) the chloromethylation condition: temperature, 40 °C; time, 3.5 h; the weight ratio of PSf to CMME, 1:4 ii) the casting condition: solvent, DMAc).

TMHDA mixture with the ratio of 3:1 shows the highest conductivity and thermal stability due to the aformentioned reason as shown in Figure 6. Water content of all the electrolytes, moreover, was in the range from 20 to 30% which was appropriate for fuel cell applications.

Optimization of Casting Solvent

To investigate the effect of solvent for casting on OH^- conductivity and thermal stability several organic solvents such as DMF, DMAc, NMP and DMSO were used from an amination step. Two amination times (*i.e.*, 90 sec and 48 h in Table 7) were employed and the ratio of TMA:TMHDA was 3:1. It is noted that the amination of CMPSf in NMP above 90 sec led to gelation and the solid-state alkaline electrolyte aminated for 90 sec had the lowest condcutivity. In case of DMSO CMPSf was not dissolved and no further amination was allowed. The two organic solvents were not appropriate for amination and casting. Figure 7 shows that the shorter amination time caused higher conductivity for DMF and DMAc. It is mainly because the shorter amination time is not enough to proceed bi-quaterization (cross-linking) but mono-quaternization. The solid-state alkaline electrolytes with the shorter amination time, however, had worse thermal conductivity. Thus the solid-state alkaline electrolyte with the longer amination time in DMAc was selected for SAFC operations and it was obtained that DMAc was the most appropriate solvent for amination and casting among the sovents.

SAFC Performance

The single cell performance was obtained as a function of the type of ionomer in electrodes. The electrodes (*i.e.*, anode and cathode) were formed by catalyst slurries comprising of catalyst, ionomer and organic solvent (sometimes with water).

Among them ionomer plays a crucial role in bridging between catalyst particle and electrolytes for mechanical binding for formation of electrodes and electrochemical connection for proton accessibility between electrodes and an electrolyte in the middle of an MEA. In fact, the use of dissimilar ionomer to an electrolyte results

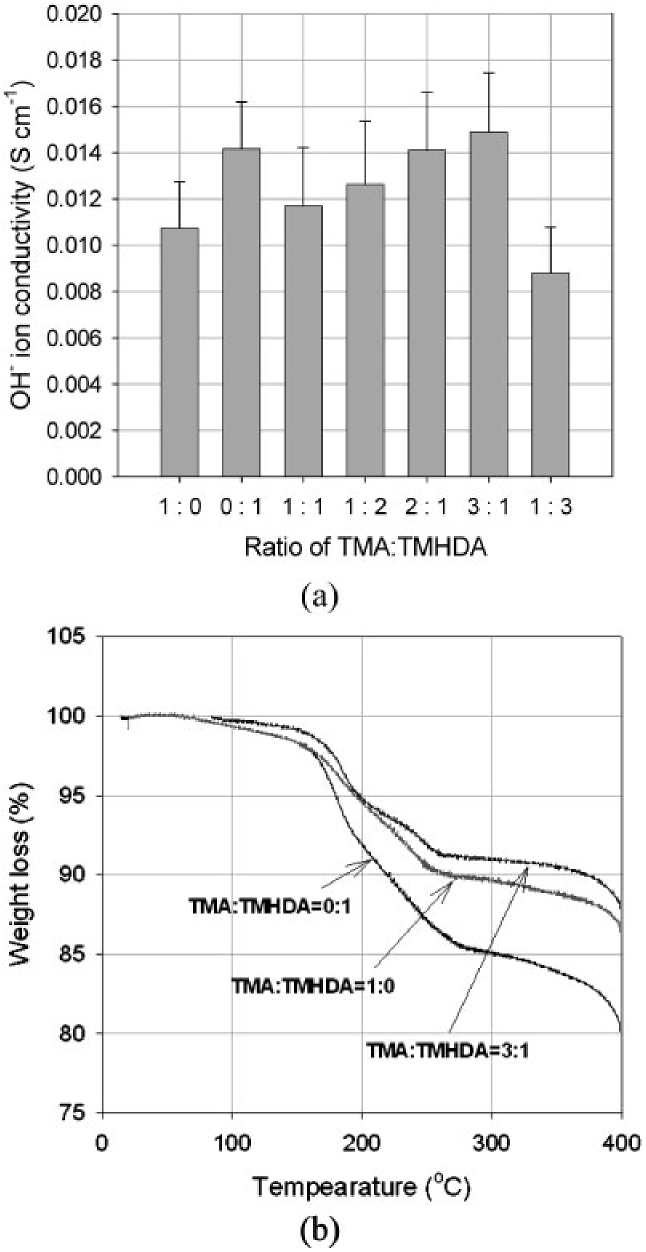

Figure 6.
(a) OH^- conductivity and (b) TGA results of solid-state alkaline electrolytes as a function of the ratio of TMA:TMHDA.

from poor adhesion and performance at the electrolyte-electrode interface. Figure 8 shows the performance results of two types of MEAs for SAFC operations. Commercially avaiable anion-exchangeable polymer used in this study was obtaind from a polystrene-based anion-exchange membrane with quaternary ammonium groups (NEOSEPTA®, Japan). Open circuit potentials (OCVs) of two types of MEAs

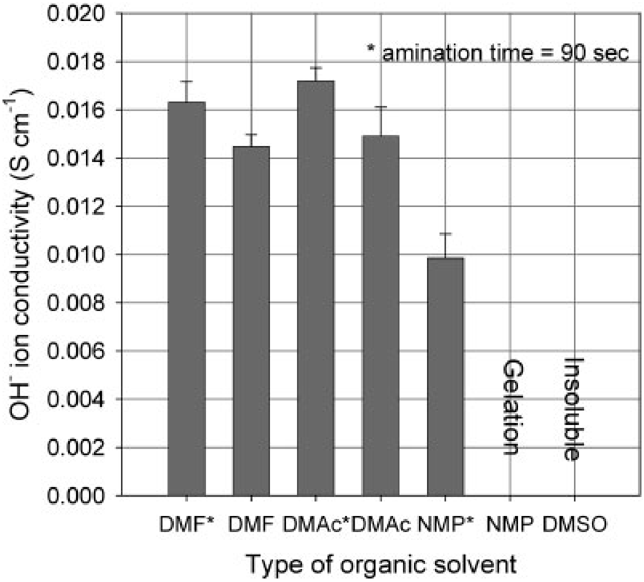

Figure 7.

Variation of OH^- conductivity as a function of casting solvent type (Fixed condition - i) the chloromethylation condition: temperature, 40 °C; time, 3.5 h; the weight ratio of PSf to CMME, 1:4 ii) the amination condition: temperature, 30 °C; time, 48 h; the weight ratio of TMA to TMHD, 3:1; the weight ratio of CMPSf to amination reagent mixture, 1:4).

were obtained above 1.0 V during the experiments. The OCV of the MEA used by the aminated CMPSf prepared in this study shows higher than one used by the commercially available anion-exchangeable polymer (Figure 8), indicating a high activation loss. It would result from more compatible attachment between electrode

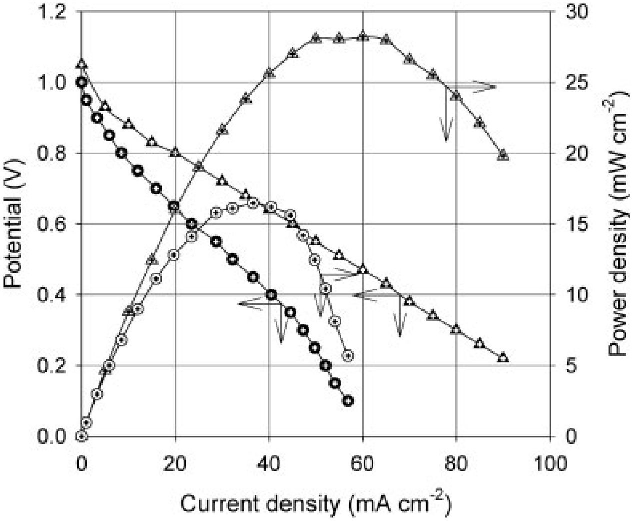

Figure 8.

Current-potential and current-power performance of SAFC operations as a function of the type of ionomer in electrodes (Circles with x-hair, made of commercially available anion-exchangeable polymer; triangles with x-hair, made of aminated CMPSf with TMA:TMHDA = 3:1).

and electrolyte due to the use of the same type of polymer. In addition there is a much higher loss in performance as current density increases for the polystyrene-based polymer due to the poor compatible attachment. The maximum power densities are shown to be 16.5 and 28.2 mW cm^{-2} at 0.45 and 0.47 V for the polystyrene-based polymer and PSf-based polymer, respectively.

Conclusions

In this study solid-state alkaline electrolytes were prepared for solid alkaline fuel cells. They were based on chloromethylated polysulfone. The amination using the optimal mixture of monoamine (TMA) and diamine (TMHDA) was allowed to improve OH^- conductivity and thermal stability, compared with the amination only using the monoamine, which is a conventional preparation for water-treatment applications. This resulted from the addition of ion-exchangeable site for OH^- ions by mono-quaternization of the diamine as well as the partial cross-linking of CMPSf by bi-quaternization of the diamine. For fabrication of MEAs the solid-state alkaline electrolytes prepared in this study could be successfully used as electrolyte and ionomer binder for SAFC.

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