Short communication

A polymethacrylate-based quaternary ammonium OH⁻ ionomer binder for non-precious metal alkaline anion exchange membrane water electrolysers

Xu Wu, Keith Scott*

School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom

HIGHLIGHTS

► A quaternary polymethacrylate ionomer with high OH⁻ conductivity was synthesized.
► This ionomer is a promising binder for catalyst layers of AAEMWE.
► Current density of the WE achieved 100 mA cm⁻² at 1.9 V with deionized water.
► The membrane electrode assembly demonstrated satisfactory stability.

ARTICLE INFO

ABSTRACT

In order to develop the alkaline anion exchange membrane water electrolysers (AAEMWE), a quaternary OH⁻ conductive ionomer binder based on polymethacrylate was synthesized by copolymerization of three kinds of methacrylate monomers, which was followed by quaternization. Tensile strength of this ionomer membrane was 7.629 MPa, with Young's modulus 0.229 GPa and elongation 45.8%. The conductivity of this ionomer could reach 0.059 S cm⁻¹ at 50 °C. With this ionomer in catalyst layers of an AAEMWE, the voltage of 1.9 V gave a current density of 100 mA cm⁻². Satisfactory stability of the membrane electrode assembly was observed from chronocoulometry.

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1. Introduction

Water electrolysers exhibit promising applications for storing energy from renewable energy sources via efficiently producing H_2, as the energy carrier [1]. There are three main kinds of water electrolysers, the alkaline water electrolyser (AWE), polymer electrolyte membrane water electrolyser (PEMWE), and the solid oxide steam electrolysers. Attributing to application of advanced solid polymer electrolyte (e.g. Nafion®) as well as modern fabrication techniques of the membrane electrode assembly (MEA), PEMWEs demonstrate much lower overpotential and higher current densities than AWEs [2]. Recent experimental results show that the voltage of PEMWEs for a current density of 1 A cm⁻² has been reduced to 1.5–1.6 V [3–5]. However in PEMWEs, precious metal

(such as platinum and iridium) loadings on the electrodes are often more than 2 mg cm⁻² [4]. High cost and availability of materials, i.e. noble metals and perfluorinated membranes, may become bottlenecks for commercialization of PEMWEs on a large scale. In terms of easier control of corrosion and cheaper materials of construction, electrolysis in basic medium is preferred over acidic medium [6–8]. In conventional figuration of AWEs, concentrated alkaline electrolytes (i.e. aqueous KOH solution) were adopted [6].

It is of potential interest to develop thinner electrolytes with fewer resistances for AWEs, i.e. OH⁻ conductive polymer membranes, to substitute KOH solutions [6–8]. Such alkaline anion exchange membrane water electrolysers (AAEMWE) could utilize only deionized water, which is similar as PEMWE. Besides, the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) will occur in high pH environment, leading to possible adoptions of various cheaper components. Moreover, the voltage and current density performance of these AAEMWEs may be much better than conventional AWEs. Firstly, it's because the application

* Corresponding author. Tel.: +44 191 2225207; fax: +44 191 2225292.
E-mail addresses: xu.wu@ncl.ac.uk (X. Wu), k.scott@ncl.ac.uk (K. Scott).

of thin AEMs may effectively reduce electrolyte resistance. Secondly, some advanced MEA fabrication methods, which have been extensively developed to improve polarization performances of PEMFCs and PEMWEs, may be applied in AAEMWEs.

Recently, oxygen evolution reaction (OER) catalysts, based on Ni [7] and Co [8], were successfully applied in experimental demonstrations of AAEMWE, which has shown promising current density performances. In our previous reports [8–10], a mature OH⁻ conductive anion exchange membrane was adopted in researches on alkaline anion exchange membrane cells, which was prepared with radiation grafting method [9]. However on the other hand, in the catalyst layers (CL) of water electrolysers, massive oxygen and hydrogen gas bubbles will generate respectively on each electrode. In our work, it's found necessary to develop novel OH⁻ conductive ionomer binders to improve the ionic conduction, mechanical stability, and morphological durability of CLs. As a part of our research work on AAEMWE, a quaternary OH⁻ conductive ionomer based on polymethacrylate was synthesized and applied in CLs of AAEMWE. The performance of a laboratory scale AAEMWE with this ionomer binder is reported in this paper.

2. Experimental

2.1. Copolymer synthesis

To synthesize the copolymer, three monomers of methacrylate: 2-dimethylaminoethyl methacrylate (DMAEMA), 2,2,2,-trifluoroethyl methacrylate (TFEMA), and butyl methacrylate (BMA), all purchased from Aldrich, were mixed in 60 cm³ toluene with a certain mol ratio in a three neck round bottom flask. The round bottom flask was placed in an oil bath at 60 °C with magnetic stirring and N₂ gas bubbling. A water cooling condenser was connected to the middle neck of the flask to reflux solvent. After adding 6×10^{-4} mol 2,2′-azobis(2-methylpropionitrile) (AIBN), the copolymerization lasted for 48 h. As shown in Fig. 1, copolymer of the three monomers, namely Poly(DMAEMA-co-TFEMA-co-BMA) (PDTB), was quaternized by reacting with CH₃I at room temperature.

2.2. Catalyst and MEA preparation

For the anode, $Cu_{0.7}Co_{2.3}O_4$ nanopowders were prepared with the method reported in reference [8]. Nickel nanopowders were purchased from Sigma Aldrich (>99% trace metal basis, <100 nm, nanopowder) and adopted for cathode. The OH⁻ conductive anion exchange membrane adopted in this study was provided by Cranfield University, which has quaternary ammonium function groups and was previously synthesized by radiation grafting [9]. The conductivity of this Cranfield-membrane was found between 0.04 and 0.076 S cm⁻¹ in the temperature range 20–60 °C. The Quaternized Poly(DMAEMA-co-TFEMA-co-BMA) (QPDTB) ionomer prepared above was applied in catalyst inks with certain contents, which worked as binder and OH⁻ conductors in CLs. Catalyst inks of cathode and anode were respectively airbrushed onto each side of the membrane. The catalyst coated on membrane (CCM) style MEA was sandwiched between two pieces of stainless steel meshes (MicroGrid® 3SS-5-050AN, Delker), which were covered with a small amount of catalyst inks for better adhesion. The catalyst loadings on the anode and cathode were respectively 3 mg $Cu_{0.7}Co_{2.3}O_4$ cm⁻² and 2 mg Ni cm⁻². This MEA was changed from
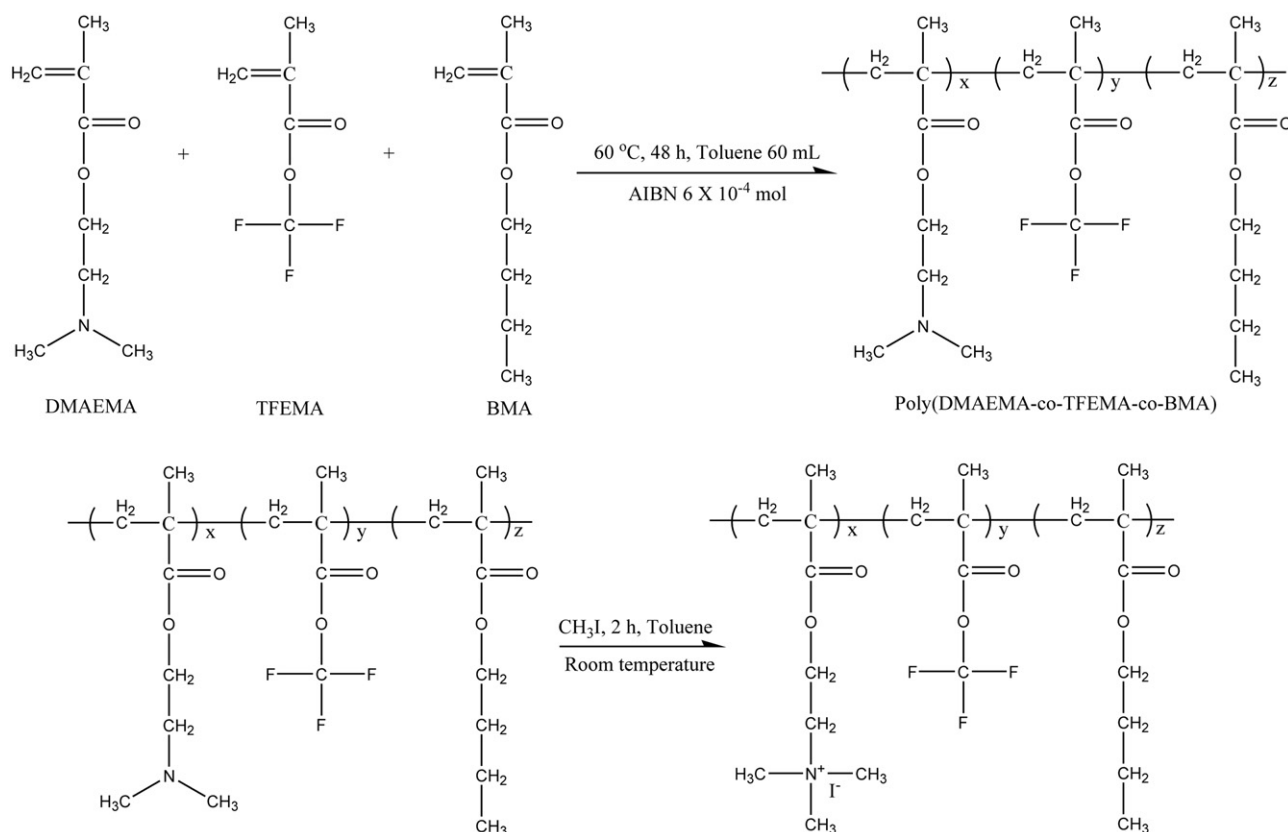

Fig. 1. Reaction scheme of synthesis and quaternization of Poly(DMAEMA-co-TFEMA-co-BMA).

halide form to OH$^-$ form by immersing it in a 0.1 mol dm^{-3} KOH solution for several hours and then rinsed with deionized water several times until rinsing water pH $\approx$ 7.

2.3. Characterizations

The PDTB copolymer was dissolved in D-chloroform and characterized with proton nuclear magnetic resonance (^{1}H NMR, at 500.16 MHz on a JEOL Lambda/Eclipse 500 MHz NMR Spectrometer). Fourier transform infrared spectroscopy (FTIR) was done with Varian 800 FTIR spectrometer system between 4000 cm^{-1} and 400 cm^{-1}. The QPDTB or PDTB in Toluene solution was casted on a glass petri dish and dried in fume cupboard at 60 °C for 24 h to form membranes, which were about 300 μm thick (Fig. 2). Tensile strength of casted QPDTB membrane in OH$^-$ form (QPDTB-OH$^-$) was characterized with an Instron 4505 tensile machine. Equivalent weight (EW) and ion exchange capacity (IEC) of the QPDTB-OH$^-$ ionomer membranes were measured by acid–base back titration [9]. The conductivity of the QPDTB-OH$^-$ membrane was measured with four point AC impedance method as described in reference [3]. Relative humidity was monitored by a temperature–humidity sensor (Vaisala HMT360) of which the probe was installed inside the conductivity measurement fixture and a N$_2$ purging humidifier at 80 °C. The morphology of MEA was investigated with scanning electron microscopy (SEM, JEOL JSM5300LV). AAEMWE single cell polarization was done with a lab-scale testing rig, as described in reference [8]. The two water chambers were filled with deionized water, which were bubbled with N$_2$ for 15 min before use. Electrochemical measurements were performed with a Voltalab PGZ100 potentiostat. The OER electrode was connected to the potentiostat as working electrode and the hydrogen side was connected to both counter and reference electrodes of the potentiostat. Polarization curve was obtained with sweep rate 1 mV s^{-1}. Electrochemical impedance spectrum was measured in a frequency range 10^5–10^1 Hz with 10 mV amplitude signal. Chronocoulometry was determined at 1.8 V for 300 min.
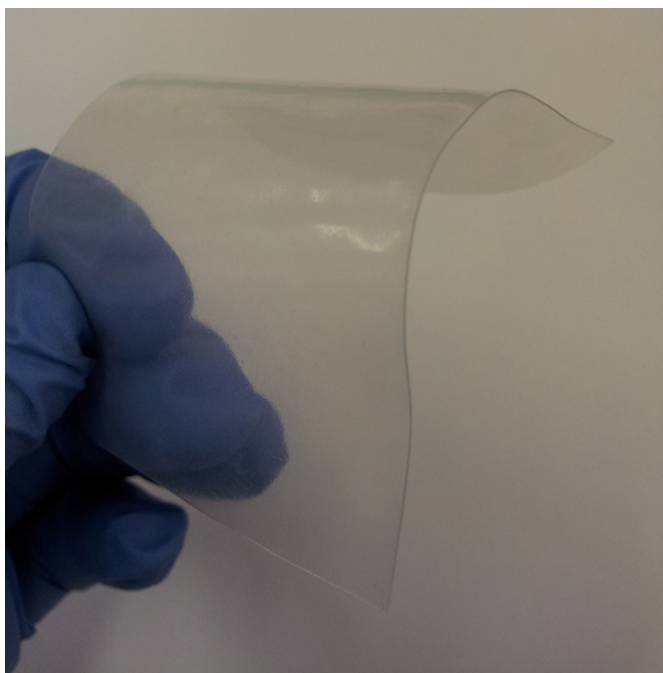
3. Results and discussion

3.1. Quaternization

Fig. 3 shows FTIR spectra of PDTB and QPDTB ionomer membranes. As shown in Fig. 3, extra peaks of QPDTB (at about 1500–1700 and 2800–3000 cm^{-1}) may be attributed to $-$N$^+$(CH$_3$)$_3$ groups. This provides some evidence of the quaternization reaction. The DMAEMA monomers were adopted in the block copolymer to provide tertiary ammonium sites for quaternization. Reactions between tertiary amino groups and appropriate alkylating agents (such as methyl halides) yield corresponding quaternary amino groups, known as the Menshutkin reaction. This way of quaternization is simple and avoids the use of some toxic quaternization agents like trimethylamine. Representative ^{1}H NMR spectra of PDTB and QPDTB polymers were shown in Fig. 4. After quaternization, characteristic peaks of $-$N$^+$$-$(CH$_3$) ($\delta$ ppm around 3.5) emerged and chemical shifts of $-$N$-$CH$_3$ (δ ppm 2.27) and $-$N$-$CH$_2$$-$ (δ ppm 2.56) of DMAEMA were weakened, indicating conversion from the dimethylamino groups to quaternary ammonium [11]. However it can be seen that dimethylamino groups were not completely quaternized from the spectrum of this QPDTB sample. This might be due to the existences of trifluoro-ethyl and butyl groups in the block copolymer which hindered the methylation of tertiary amine by methyl iodide (CH$_3$I). Probably, higher temperature and longer reaction time are required to increase reactivity of this Menshutkin reaction. The quaternary PDTB ionomer in iodide form could be transferred to OH$^-$ form by treating with KOH solution (0.1 mol dm^{-3}) at room temperature for several hours.

Chemical stability of alkyl quaternary ammonium function groups is a main issue in the development of alkaline anion exchange membranes [12]. In concentrated alkaline solutions, the $-$N$^+$$-$(CH$_3$) groups of QPDTB are instable because with the attack of OH$^-$ anions and heat, degradation of the quaternary ammonium groups would take place via Hofmann elimination reaction and/or direct nucleophilic substitution. In this study, deionized water was applied in the water electrolyser testing fixture rather than a KOH solution. Also for satisfactory durability AAEMWE tests were performed in a temperature range 20–30 °C.

3.2. Ionomer properties

On one hand, the mechanical properties of the block copolymer were adjusted by varying the mol ratio of the three monomers. On
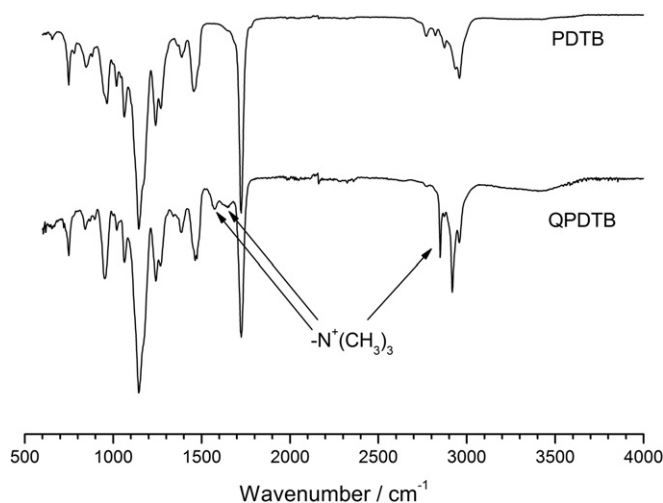
Fig. 2. A sample piece of QPDTB ionomer membrane.
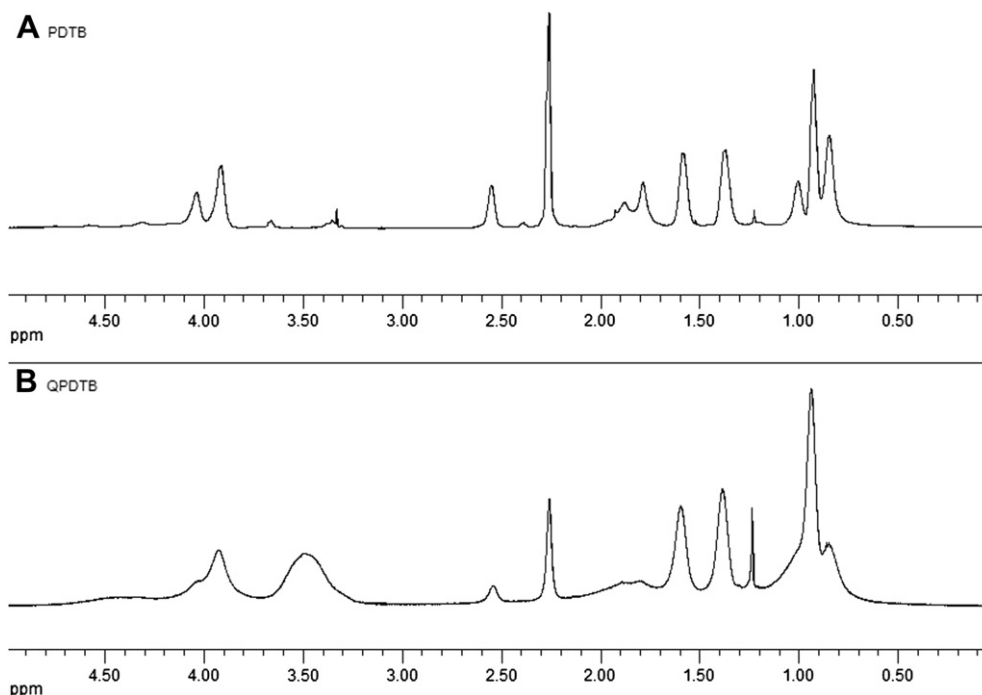
Fig. 3. FTIR spectra of PDTB and QPDTB.

Fig. 4. ^{1}H NMR spectra in D-chloroform of (A) PDTB and (B) QPDTB.

the other hand, the ionic conductivity of the copolymer depends on the amount of quaternary ammonium functional groups, which is mainly related to the content of DMAEMA monomer. In literature, the tensile strength of pure poly(DMAEMA) was found to be only 1.5 ± 0.2 MPa [13]. Besides, quaternized poly(DMAEMA) polymers usually dissolve in water [14], which handicapped the practicality of pure quaternized poly(DMAEMA) ionomer in catalyst layers of water electrolysers. Incorporating methacrylate monomers with fluorinated alkane side chain (such as TFEMA) may improve the hydrophobicity of the copolymer. Besides, the BMA content could adjust both hydrophobicity [15] and mechanical strength [16] of the copolymer, due to its longer alkane chain. The tensile strengths of QPDTB membrane with 41 mol% DMAEMA were determined and the stress-strain curve is shown in Fig. 5. The tensile strength of this membrane was 7.629 MPa, which is five times higher than pure poly(DMAEMA) membrane. Its Young's modulus was 0.229 GPa in the initial strain region, indicating good resistance to deformation of the polymer. The elongation at rupture point was 45.8%. Besides, the necking region of the stress–strain curve indicates QPDTB a tough and ductile polymer, which may possess better morphology stability than brittle polymers.

In an AAEMWE [8], deionized water is typically supplied to each side of the MEA, which provides suitable hydration for ionic conduction of the membrane and catalyst layers. Ionic conductivity of QPDTB ionomer membranes (with 26 mol% and 41 mol% DMAEMA) in OH^- form was investigated at a relative humidity (RH) 97–105%, as shown in Fig. 6. Conductivity of the QPDTB membrane with 26 mol% DMAEMA increased from c.a. 0.015 S cm^{-1} to c.a. 0.025 S cm^{-1} when the temperature increased from 20 °C to 50 °C. The other one with 41 mol% DMAEMA exhibited higher conductivities and could reach about 0.059 S cm^{-1} at 50 °C. The apparent activation energy of the two samples in Fig. 6 was respectively about 16.41 kJ mol^{-1} for the one with 26 mol% DMAEMA and 22.02 kJ mol^{-1} for the one with 41 mol% DMAEMA. IEC (EW) of the QPDTB-OH$^-$ membranes with 26 mol% and 41 mol% DMAEMA was respectively 0.867 (1153) and 1.275 meq g^{-1} (784 $g_{polymer}$ n_{OH}^{-1}).

Further increasing the content of DMAEMA might further improve the conductivity of the ionomer but may also increase its hydrophilicity. Solubility in water was observed in this study for QPDTB copolymers with DMAEMA content more than 50%.

3.3. AAEMWE performance

In fuel cells the current collectors are usually gas diffusion carbon fibres or carbon papers, which are placed as close as possible with catalyst layers. However, so far as durability is concerned, carbon-based current collectors (or connectors) for water electrolysers are not suitable for the OER electrode due to anodic corrosion of carbon. Especially in the alkaline system, corrosion of carbon may lead to CO_2 and carbonyl groups which may instantly
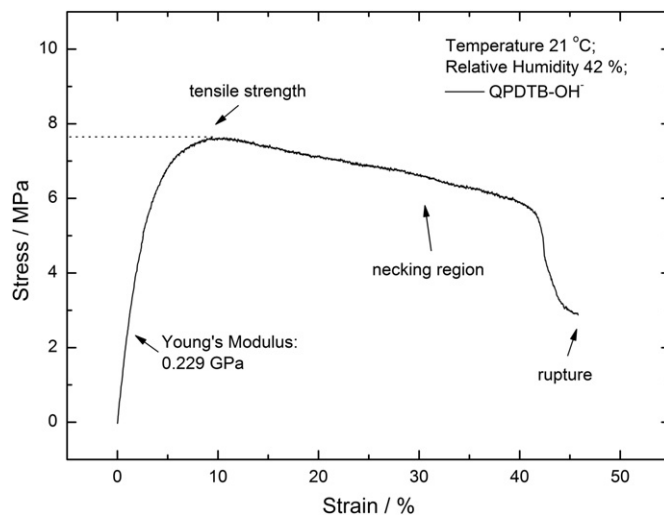

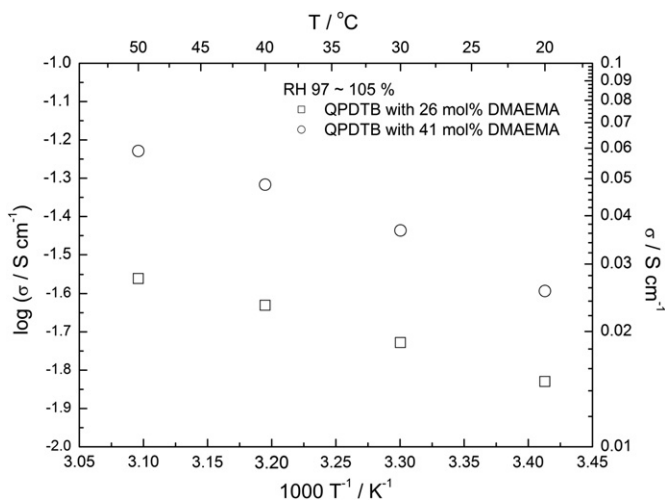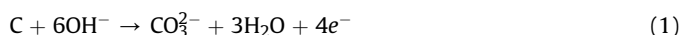**Fig. 5.** Tensile strength of QPDTB-OH$^-$ ionomer membrane.

Fig. 6. Arrhenius plots of QPDTB-OH⁻ ionomer membranes.

Fig. 8. Polarization curves of AAEMWE: straight line is experimental data and dash line is IR corrected data, inset figure is EIS at 2.1 V.

neutralize the OH⁻ ion of the quaternary ammonium groups irreversibly [17]:

$$C + 6OH^- \rightarrow CO_3^{2-} + 3H_2O + 4e^- \tag{1}$$

Therefore, non-carbon materials like stainless steel mesh were adopted in our AAEMWE as current connectors. The morphology of the surface of MEA was investigated with SEM. As shown in Fig. 7 the stainless steel mesh was bound onto the surface of catalyst coating, which contains QPDTB-OH⁻ ionomer and $Cu_{0.7}Co_{2.3}O_4$ nanopowder catalyst. Catalyst coating was also seen on the enlarged figure of the mesh surface (Fig. 7B), which is because the meshes were treated with catalyst ink before being bound to the CLs. This method resulted in good adhesion between the meshes and CLs.

Preparation of the MEA of water electrolysers may have major influences on its current density performances [3–8]. The catalyst layers of the MEA are normally either coated on the membrane (namely CCM method) or coated on gas diffusion layers (namely CCG method). In this study MEAs were prepared with CCM method, which might effectively reduce the ionic resistance between catalyst layer and the membrane. Since there is not any gas diffusion layers in this MEA, the catalyst layers should be enough hydrophobic and porous. In other words, there should be enough channels for gases bubbles generated on the catalyst surface to quickly leave CLs and for sufficient water to refill CLs. In this work, hydrophilicity of QPDTB ionomer was enhanced by incorporating the trifluorinated methyl groups in the copolymer. Good tensile
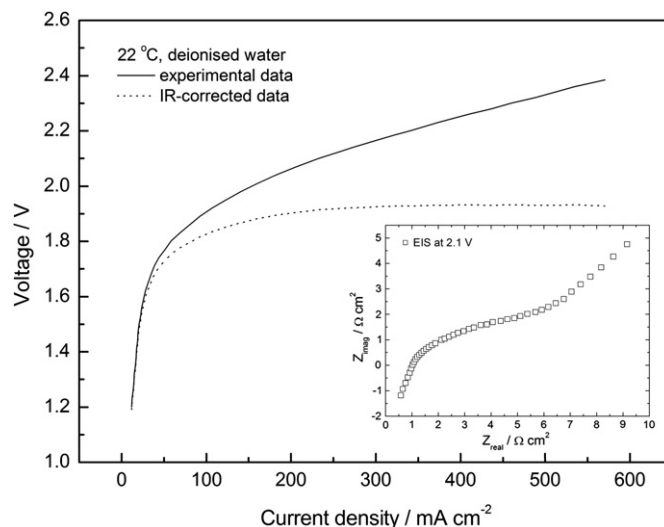
properties of QPDTB would also lead to good morphology durability of CLs, which is also important for MEA's stability [4,8].

Polarization curve of a practical AAEMWE at room temperature is shown in Fig. 8. IR correction was done by deducting the electrolytic resistance. The total electrolytic resistance of MEA (about 0.85 Ω cm²) was determined by the intercept in the EIS data, on the real axis in the high frequency region, as shown in the inset figure of Fig. 8. The onset voltage of electrolysis was about 1.65 V, which however was followed by large activation overpotential, i.e. the exponential region, indicating it necessary to further improve the catalyst–ionomer interface in the three phase boundary [4]. The voltage for a current density of 100 mA cm⁻² was about 1.9 V, which is similar with results of recent publications [8,10]. The current density performance could have been better if KOH solution was employed instead of deionized water or increasing operation temperature, which however would actually lead to poor stability of the QPDTB ionomer. Although current density and overpotential performances of AAEMWE at the current stage are not as good as those for PEMWEs [3–5], AAEMWE devices can be made with larger electrode areas to achieve equal rates of H₂ production with PEMWE since the material costs of AAEMWE are much less than PEMWE. Actually for both PEMWE and AAEMWE stability is one of the main issues. Stability of the AAEMWE of Fig. 8 was demonstrated by chronocoulometry data shown in Fig. 9. It can be seen that the current density was reasonably stable for continuous operation for 300 min.
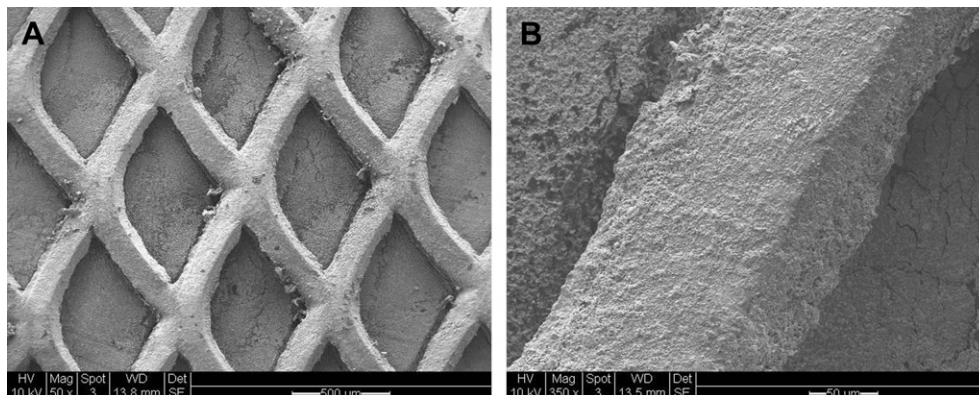

Fig. 7. SEM of (A) QPDTB-OH⁻ ionomer bound $Cu_{0.7}Co_{2.3}O_4$ catalyst layer surface with stainless steel mesh, (B) enlarged surface of stainless steel mesh.
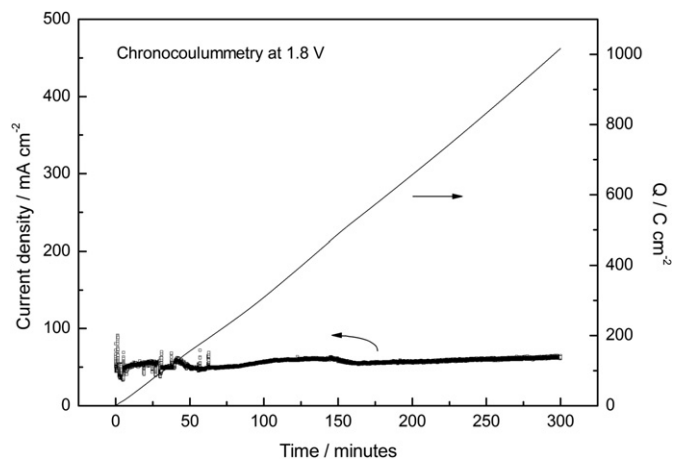
Fig. 9. Chronocoulometry of the AAEMWE in Fig. 8 at 1.8 V for 300 min.

4. Conclusions

This paper reports an OH$^-$ conductive quaternized Poly(DMAEMA-co-TFEMA-co-BMA) copolymer with alkyl quaternary ammonium groups as a promising ionomer binder for catalyst layers of AAEMWE. The synthesis and quaternization of this copolymer were studied with FTIR and NMR. This QPFTB ionomer exhibited good mechanic properties and high ionic conductivity in OH$^-$ form. The MEA using this ionomer as binder in CLs exhibited good current density performances and promising stability. In subsequent works, ionic conductivity and mechanic property of this kind of OH$^-$ conductive ionomer may be further improved by changing the methacrylate monomers. Also, more attention shall be given to the catalyst–ionomer interface of CLs in order to improve current densities.

Besides, adoption of stainless steel mesh in this study may avoid degradation of the ionomer according to Equation (1). However the stainless steal mesh may still suffer corrosion at high voltages so development of the current connector would be necessary in future works. Currently a major issue of AAEM is about the chemical stability of quaternary ammonium groups. For better stability of the ionomer, enduring attacks of OH$^-$ and heat (Hofmann elimination), using alternative function groups for OH$^-$ conduction to substitute the quaternary ammonium is becoming increasingly topical.

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