An Acrylate-Polymer-Based Electrolyte Membrane for Alkaline Fuel Cell Applications

Yanting Luo,[a] Juchen Guo,[a] Chunsheng Wang,*[a] and Deryn Chu[b]

Alkaline fuel cells (AFCs) recently attracted renewed attention because of their potential to surpass proton exchange membrane fuel cells (PEMFCs). The long-existing issues of PEMFCs, including expensive noble-metal catalysts and polymer electrolytes,[1] as well as CO poisoning and inferior temperature endurance,[2] prevented them from being used in a broad range of applications.[3] Contrarily, advantages of AFCs include fast kinetics in the reduction of the oxidizing agent[4] and the possibility to use base-metal catalysts.[5] However, a critical challenge for conventional AFCs is the use of aqueous alkaline electrolytes, which can react with CO₂ from air to form carbonate salts (e.g., K₂CO₃). As a result, the performance of the fuel cell would quickly deteriorate. To solve this problem, recent investigations focused on intrinsically OH⁻-conducting alkaline polymer electrolyte (APE) materials to replace the alkaline electrolytes. By using APEs, the formation of carbonate salts can be prevented, which is attributable to the absence of metal ions. However, carbonate ions might still be formed through a reaction with CO₂, which would result in a reduced OH⁻ conductivity.[5–7] Application of APEs can also enable a compact design[8] and eliminate corrosion from alkaline solutions. These advantages confirm that APE fuel cells (APEFCs) present a very promising energy conversion technology. Because APEs are a key component determining the ultimate performance, they should exhibit a high OH⁻ conductivity and superior mechanical properties, and in addition be of low cost.[9]

To date, the most common synthesis route for APEs is chloromethylation of polymers having a phenyl structured backbone, which is followed by quaternization. Many polymers have been used as precursors to synthesize APEs, including polysulfone,[10–12] poly(arylene ether sulfone),[13] polyetherketone,[14] poly(ether imide),[15] polyethersulfone cardo,[16] poly(phenylazinon ether sulfone ketone),[17] poly(dimethyl phenylene oxide),[18] and poly(phenylene). Also, a recent study by Lin and co-workers[20] reported high conductivity and mechanical strength for an alkaline polymer electrolyte based on a cross-linked ionic liquid. The phenyl backbones of the polymers have in common that they are all excellent engineering polymers exhibiting good mechanical properties because of rigid ring structures. However, this advantage can be seriously weakened by the chloromethylation–quaternization process, which converts the polymer from an ionic insulator into an ionomer and thus, from hydrophobic to hydrophilic. As a result of the hydrophilicity, the mechanical properties of the APEs in the humid working environment of a fuel cell can be very different from that of the precursors. Because their backbones consist of aromatic groups, these precursor polymers can be modified to exhibit extreme hydrophilicity through the chloromethylation–quaternization process. The resulting APE may have a very high anionic conductivity, but with very poor mechanical properties in humid environment. Therefore, an obvious shortcoming of the chloromethylation–quaternization process is the difficulty to control the degree of chloromethylation and quaternization precisely,[21] thus making it difficult to balance conductivity and mechanical properties. Cost is also a concern, since the aforementioned APE precursors are high-cost polymers because of the sophisticated synthesis process.[22]

In a previous study, we reported a novel APE made from poly (methyl methacrylate-co-butyl acrylate-co-vinylbenzyl chloride) (PMBV).[7] This copolymer was synthesized using solution-free radical polymerization. Xu and co-workers also reported an independent study on APE made from a copolymer using similar polymerization methods.[23] Although this copolymer exhibits a promising performance, our previous study encountered two problems: The three monomers, methyl methacrylate (MMA), butyl acrylate (BA), and 4-vinylbenzyl chloride (VBC), have different reactivity ratios so that they polymerize at different reaction rates. Because of the slow diffusion of propagating copolymer chains and the diluted monomer concentration in the polymerization solution, the monomers with lower reactivity ratios have a smaller possibility for complete conversion. Therefore, the copolymer composition did not match the designed monomer ratio. The second concern is that the molecular weight of the copolymer in our previous study was not as high as expected, which could considerably weaken the mechanical strength. To address these problems, we demonstrate a novel bottom-up synthesis of PMBV by using mini-emulsion polymerization for the first time. Unlike chloromethylation of existing polymers, we synthesized PMBV by using various monomers selected to meet the specifications for conductivity and mechanical strength. Specifically, VBC (15 mol %) contained the chloromethyl functional group, which could be quaternized and then successively ion-exchanged to obtain OH⁻ conductivity.[24] Polymerized MMA exhibits a high rigidity and toughness. As a result, the MMA monomer (80 mol %) was chosen to provide mechanical strength. The brittleness inherent to MMA and VBC was overcome by adding a small portion of BA (5 mol %), which conferred flexibility to the resulting APE.

[a] Y. Luo, Dr. J. Guo, Prof. Dr. C. Wang
Chemical and Biomolecular Engineering
2113 Chemical and Nuclear Engineering
University of Maryland, College Park, MD 20742 (USA)
Fax: (+1) 301-314-9126
E-mail: cswang@umd.edu

[b] Dr. D. Chu
Sensors and Electron Device Directorate
US Army Research Laboratory
Adelphi, MD 20783 (USA)

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The mini-emulsion polymerization (see the Supporting Information for mechanism schematics and polymer characterization) is a unique emulsion polymerization technique. High shear force (e.g., sonication) is usually employed to disperse monomers in an aqueous phase as droplets. Compared to conventional emulsion techniques, the monomer droplet size is much smaller (a few hundreds of nanometers), and the droplet size distribution is much more uniform. Because of the high surface area of the monomer droplets, all surfactants are adsorbed on the droplet surface to stabilize the dispersion. Moreover, small amounts of an extremely hydrophobic non-active reagent (e.g., hexadecane) dissolved in the monomer droplets are also used as co-stabilizer to further prevent Ostwald ripening. Polymerization is primarily through radical (primary or oligomeric) entry into monomer droplets, when water phase initiator is employed. In mini-emulsions, each monomer droplet can be considered as an individual reactor for bulk polymerization. Because of the small reactor (i.e., droplet) size, the effect of slow diffusion of the propagating chains can be reduced, and high monomer conversions can be achieved. Therefore, the composition of obtained copolymer is in good agreement with the monomer ratio. Also, high molecular weights can be achieved through mini-emulsion polymerization using mild conditions, thus eliminating the difficulties in mixing and heat management in bulk polymerizations. Moreover, water was used as the reaction medium in this mini-emulsion copolymerization, which made it environmentally friendly.

In our experiment, 97% overall monomer conversion was achieved after 120 min reaction (Figure S2 in the Supporting Information). The molecular weight of the obtained PMBV copolymer was 1.5 × 10^6 g mol⁻¹ (Figure S3), which is six times higher than that of the copolymer in our previous study. The composition of the resulting PMBV was 78.8:4.8:16.4 (molar % of MMA/BA/VBC) according to calculations based on the ¹H NMR spectrum (Figure S4). This composition is in good agreement with the monomer ratio in the reactant mixture (80:5:15). The glass transition temperature (T_g) of the PMBV copolymer was 102 °C as determined by using differential scanning calorimetry (DSC, Figure S5), which is in agreement with results calculated from measurements performed at 93 °C and based on the composition.

The complete synthesis route for the APE (see the Supporting Information for details of membrane preparation and characterization) is shown in Scheme 1. Firstly, the PMBV copolymer was synthesized by using mini-emulsion polymerization. This was followed by quaternization of PMBV by reaction with trimethylamine (Me₃N) in dimethylformamide (DMF). The quaternized PMBV (QPMBV) was then cast to obtain a membrane and soaked in 6 M KOH at room temperature for 24 h to exchange Cl⁻ with OH⁻. After ion-exchange, the polymer membrane was washed with abundant water until pH7 was reached. The final product, QPMBV-APE, was obtained after drying was completed. Elemental analysis revealed complete quaternization (all VBC groups were quaternized). The products for each synthesis step are shown in Figure 1. Acid-based back-titration measurements indicated an ion-exchange capacity (IEC) of 1.28 mmol g⁻¹, and the efficiency of ion-exchange was estimated to be approximately 90% (see the Supporting Information). The nature of conducting ions in QPMBV-APE was identified by using a titration method (Figure S8). The titration results indicated that most of the conducting ions (OH⁻) were converted to HCO₃⁻ and/or CO₃²⁻ approximately 60 min after QPMBV-APE was neutralized. The stability of the conductivity at high pH values was also tested in a 6 M KOH solution (Figure S9). The stability test indicated a 3.3% decrease in the IEC of QPMBV-APE being soaked in 6 M KOH solution for 7 days.

Both water uptake and anionic conductivity of the QPMBV electrolyte membranes were measured under fuel-cell operation.
tion conditions [80% relative humidity (RH) and 40–70 °C]. Figure 2 depicts the water uptake of the QPMBV-APE mem-
brane at 80% RH as a function of temperature. The results are based on triplicate measurements. The water uptake at 80% 
RH was between 20 and 30 wt% in the temperature range from 40 to 70 °C.

The anionic conductivity of QPMBV-APE was measured in a 
four-probe testing cell (BekkTech, BT-112) by using electro-
chemical impedance spectroscopy (EIS, Figure S7). Figure 3 
shows the development of the conductivities in a temperature 
range from 50 to 80 °C and at 80% RH. The calculated activa-
tion energy was 52.2 kJ mol⁻¹. The high anionic conductivity of 
QPMBV-APE of up to 43 mS cm⁻¹ could be attributed to 
15 mol% anions attached to the VBC group in the copolymer.

Prior to performance tests of fuel cells using APE (APE-FC), a
membrane electrode assembly (MEA) was fabricated following 
the standard procedure detailed in the experimental section[31] 
by using a 50 μm thick QPMBV-APE membrane as electrolyte
and QPMBV in an ethanol/water solution as ionomer. Pt was 
used as a catalyst using a loading of 0.4 mg cm⁻². Hydrogen 
and oxygen were used as the fuel and oxidant, respectively, at 
100 ± 2 sccm (standard cm³ min⁻¹). The performance of the 
QPMBV-APE fuel cells was tested at 80% relative humidity (RH) 
at various temperatures by using a current scan rate of 
3 mA s⁻¹ and a back pressure of 10⁵ Pa. The use of a low-cur-
rent scan rate was to ensure that the fuel cell performance
reached steady state. As shown in Figure 4, the initial voltage 
drop (≈ 100 mV) was mainly attributable to an activation loss 
of the interfacial electrochemical charge-transfer reaction in 
the catalyst layer of the MEA.[32] After the initial activation loss, 
the fuel cell voltage deceased gradually with an increase in 
current density. The fuel-cell performance was improved when 
the temperature increased from 50 to 70 °C. At 70 °C, the cur-
tent density reached 500 mA cm⁻², and the fuel cell could de-
deliver a peak power density of 180 mW cm⁻². Even at lower tem-
peratures (60 °C and 50 °C), the fuel-cell performance using 
QPMBV-APE had maximum power densities of 160 and 
115 mW cm⁻², respectively. This is among the best performan-
ces reported for APE membranes.[20, 33–36] The energy output 
as approximately four times higher than in our previous 
study.[20] This improvement can be attributed to the fivefold in-
creased anionic conductivity and the twofold thinner mem-
brane used. Although the Pt catalyst loading was smaller, 
these improvements give rise to a better performance.

In conclusion, a novel APE was synthesized through mini-
emulsion copolymerization with designed hydrophobic and 
hydrophilic (anion conducting) segments to balance conductiv-
ity with mechanical strength. Our results indicated that the in-
tentionally incorporated VBC functional groups were almost 
completely quaternized and ion-exchanged. The exceptional 
APE-FC performance revealed the great potential of QPMBV-
APE. Not only was a promising APE synthesized, but this study 
also demonstrated a novel concept: alkaline polymer electro-
lytes can be designed bottom-up through mini-emulsion poly-
merization by precisely selecting the functional monomers.

Figure 2. Water uptake by the OH⁻-exchanged QPMBV-APE membrane as a function of temperature at 80% RH.

Figure 3. Conductivity of the QPMBV-APE membrane as a function of temperature at 80% RH.

Figure 4. i-V polarization curves of the QPMBV-APE-FC at 80% RH (● 50 °C; 
▲ 60 °C; ● 70 °C).
The conductivity and mechanical durability of the APE can be tailored by selecting desirable monomer and controlling the polymerization process. In this way, both properties can be improved without compromising the other. Furthermore, the mini-emulsion copolymerization process can be used to synthesize high molecular weight APEs with superior mechanical properties. Control of the polymerization process, such as step-wise monomer feeding, can be used to introduce favorable polymer chain sequences that could lead to hydrophobic and hydrophilic micro-phase separation. This will the subject of future studies.

**Experimental Section**

**Mini-emulsion copolymerization**

The mini-emulsion was prepared by dispersing a mixture of monomers (30 g) with a designed molar ratio (MMA/BA/VBC = 80:5:15) and hexadecane (0.12 g) in an aqueous sodium dodecyl sulfate solution (SDS, 0.01 mol L⁻¹, 150 mL) by applying ultrasonic shearing to form a stable mini-emulsion using a homogenizer (Omni Sonic Ruptor 400) at 30% power output for 9 min. The polymerization was initiated by injection of the initiator potassium peroxysulfate (KPS) (0.01 mol L⁻¹ in the water phase) into the mini-emulsion at 70 °C under a nitrogen atmosphere. The reaction was terminated after 4 h by quenching in an ice bath. The copolymer was filtered and dried in a fume hood overnight and was further dried in a vacuum oven at 60 °C for 24 h.

**Membrane preparation**

The obtained PMBV was dissolved in dimethylformamide (DMF) at 80 °C and quaternized using trimethylamine (Me₃N, Sigma–Aldrich) with OH⁻ to exchange Cl⁻ with OH⁻. The OH⁻-exchanged membrane was washed with deionized water until pH7 was reached.

**Fabrication of the membrane electrode assembly (MEA)**

Carbon paper (Toray, TGP-H-60) was first brushed by using a PTFE/Fabrication of the membrane electrode assembly (MEA) solution in an ethanol/water mixture (50/50 vol %) by sonication. The Pt/C catalyst dispersion was sprayed onto the processed carbon paper giving a Pt loading of 0.4 mg cm⁻². Then the QPMBV-APE membrane was sandwiched between two catalyst-loaded carbon papers (5 cm²) by using a hot-press (Carver 973214 A) under a pressure of 2 x 10⁸ Pa at 60 °C for 10 min to obtain the MEA for the performance test.

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