Electronic Supplementary Information (ESI)

Highly Stable Self-Crosslinked Anion Conductive Ionomers for Fuel Cell Applications

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1. Materials.

4,4'-Difluorophenyl sulfone, 4,4'-difluorobenzophenone, bisphenol A (BPA), allyl bromide and N-Bromosuccinamide (NBS) were purchased from Sigma Aldrich, Inc.. Formaldehyde, trimethylamine aqueous solution (35wt %), benzoyl peroxide (BPO), *N*,*N*'-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), toluene and methanol were purchased from Spectrochem, India, and used with proper purification. Chloroform, potassium carbonate, sodium bicarbonate, sodium hydroxide, ethanol, and acetone (AR grade) were obtained from SD Fine Chemicals, India. Nitrogen, Argon gases were purchased from Ultra-Pure Gases (I) Pvt. Ltd., India.

2. Synthesis of bromo substituted 2,2'-diallylbisphenol (ABP-Br) monomer.

a) Synthesis of 2,2'-diallylbisphenol monomer (ABP). The ABP was synthesized by the formation of allyl phenyl ether followed by Claisen rearrangement. BPA (0.2 mol) reacts with allyl bromide (0.43 mol) in presence of K_2CO_3 in acetone solvent for 15 h at 50 ^oC.[1] After filtration of excess K_2CO_3, solvent was removed under vacuum. Viscous oily liquid of allyl phenyl ether was obtained. The ABP was prepared by the Claisen rearrangement of allyl phenyl ether (10 mmol) with zinc powder (5.0 mmol) in THF at 55 ^oC for 4 h.[2]

b) Synthesis of bromo substituted 2,2'-diallylbisphenol (ABP-Br) monomer.

ABP (5 mmol) was refluxed with NBS (40 mmol) in presence of radical initiator such as BPO under inert atmosphere in chloroform (100 mL) for 6 h. The reaction solvent was completely evaporated under reduced pressure and pale yellow colored compound of ABP-Br was obtained.[3] The synthesized ABP, ABP-Br monomers were characterized by ^{1}H NMR spectra (Figure S1(a) and S1(b), respectively).

3. Synthesis of 2,2',3,3'-tetrakis(chloromethyl)bisphenol (TCMBP) monomer.

A 300 mL round-bottomed flask was charged with bisphenol-A (40 mmol), K_2CO_3 (100 mmol) and water (200 mL) containing 37% formaldehyde (740 mmol) under constant stirring in an inert atmosphere at 60 °C for 4h. CO_2 was bubbled through yellow coloured solution at 30^{o}C until it turned to cloudy. The reaction mixture was extracted with ethyl acetate and dried in $MgSO_4$ followed by removal of solvent under reduced pressure. The residue obtained (2,2',3,3'-tetrakis(hydroxymethyl)bisphenol (THMBP) was diluted with $CHCl_3$ followed by drop-wise addition of $SOCl_2$ (120 mmol) solution in $CHCl_3$ (100 mL) over 30 minutes. Above solution was stirred for 1 h and washed with saturated $NaHCO_3$ solution to remove excess of $SOCl_2$. Now the organic layer was dried ($MgSO_4$) and solvent was removed under reduced pressure. The obtained viscous oily product was solidified to obtained 2,2',3,3'-tetrakis(chloromethyl)bisphenol (TCMBP) monomer. The structure of synthesized monomer was confirmed by ^{1}H NMR spectra (Fig. S1(c)). Different degree of chloromethylation (DCM) (90%, 55% and 35%) estimated by ^{1}H NMR spectra of TCMBP monomer were synthesised under various reaction conditions as given in Table S1.

4. Synthesis of Self-Crosslinked anion conductive ionomers (SCL-ACIs).

FPS (11.5 mmol), ABP-Br (5.5 mmol), TCMBP (5.5 mmol), potassium carbonate (6.0 mmol), calcium carbonate (60 mmol), DMAc (80 mL), and toluene (20 mL) were charged into three neck round bottom flask equipped with Dean-Stark trap and nitrogen inlet. The reaction mixture was heated to 140 °C for 3h. After complete evaporation of toluene; the temperature was slowly increased to 170 °C for another 6h. After cooling of reaction mixture, required quantity of TMA was added under stirring at 55 ^{o}C for 8 h followed by precipitation in deionized water and washing with chilled methanol to obtain SCL-ACI-Cl copolymer.

5. Membrane Preparation

Before the preparation of membrane, the obtained SCL-ACI-Cl copolymer was dipped into 1M KOH for 24 h at room temperature to convert into SCL-ACI-OH copolymer. In spite of self-crosslinking, ACI membrane was obtained by dissolving SCL-ACI-OH copolymer (1.0 g) in 7 mL NMP at 70-80 ^{o}C may be due to the presence of more hydrophilic moieties and cast onto a clean glass plate followed by drying under vacuum at 90 °C for 24 h.

Structure of SCL-ACI-90 copolymer was characterized by ^{1}H NMR spectrum (Figure S2). The peaks at 1.51-1.73 ppm corresponded to $–C(CH_3)_2$ (denoted by b, b'). The peak at 3.14 ppm (assigned as k) attributed to the methyl protons of ammonio groups, while peaks at 5.17, 5.32 ppm (assigned as i, j) corresponded to two vicinal methylene groups (ammonio groups). The aromatic protons of diphenyl sulfone, TCMBP and ABP-Br moieties correspond to 6.69-7.93 ppm chemical shift values (as designated in the Figure S2). The crosslinked ═CH showed peak at δ 5.94 ppm (assigned as c) and $–CH_3$ group attached to ═CH showed peak at 2.36 ppm. From all the above observations, the structure of crosslinked SCL-ACI-90 was confirmed (Figure S2).

6. Measurements.

The ^{1}H NMR was recorded by NMR spectrometer (Bruker, 200& 500 MHz for ^{1}H NMR) in deutrated acetone or DMSO-d_6 (deutrated dimethylsulfoxide) with reference to tetramethylsilane. The mechanical properties of the developed SCL-ACIs were analysed by Zwick UTM instrument in dry condition at 30^{o}C.

7. Conductivity.

Membrane hydroxide conductivity of AMBPE membranes were measured by potentiostat/galvanostat frequency response analyzer (Eco Chemie, B.V. Utrecht, The Netherlands Auto Lab, Model PGSTAT 302N). The membrane was sandwiched between two in-house made stainless steel circular electrodes (4.0 cm^2). Direct current (dc) and sinusoidal alternating currents (ac) were supplied to the respective electrodes for recording the frequency at 1 μA/s scanning rate within 10^6 to 1 Hz. The membrane resistance was determined from Nyquist plots using Fit and Simulation method. Membrane resistance (R^{m}) was measured in equilibration with deionised water and membrane conductivity (σ) was estimated by the following equation,

$$\sigma_{\text{OH-}} = \frac{\Delta x}{A R^{\text{m}}} \qquad (1)$$

Where Δx and A are the membrane thickness and membrane conducting area respectively. Membrane conductivity data at different temperatures under 100% relative humidity (RH) was used for the estimation of activation energy (E_a) by following expression:

$$E_a = -b \times R \qquad (2)$$

Where b is the slope of the regression line of ln σ (S cm^{-1}) vs 1000 T^{-1} (K^{-1}) plot and R is the gas constant (8.314 J K^{-1} mol^{-1}).

8. Water Uptake and Swelling Ratio.

The membrane water uptake *(WU)* was determined by dipping the membrane in distilled water for 24 h and the wet weight was recorded after removing surficial water. Then the wet membranes were dried under vacuum at 80°C until to get a constant weight and thus dry weight of the membranes were recorded. The water uptake (*WU*) and Swelling Ratio (%) of the membranes was determined using the following eq. (3) & (4)

$$WU\ (\%) \ = \ \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (3)$$

Where W_{wet} and W_{dry} are the masses of the membrane under wet and dry conditions.

$$Swelling\ Ratio\ (\%) \quad = \quad \frac{T_{wet} - T_{dry}}{T_{dry}} \times 100 \quad (4)$$

Where T_{wet} and T_{dry} are the thickness of the membrane under wet and dry conditions.

9. Ion-exchange capacity (IEC)

AMs were equilibrated in 50 ml of 0.1MNaCl solution for 24 h; IEC was determined by acid–base titration of equilibrated NaCl solution by using the following eq.

$$IEC\left(m\,equiv./g\ of\ dry\,membrane\right) = \frac{C_{OH^-}\,V_{sol}}{W_{dry}} \qquad (5)$$

Where C_{OH}^{-} the concentration of OH^- in the extraction solution and W_{dry} is the dried membrane weight.

10. Methanol permeability and Selectivity parameter

Methanol permeability (P_m) of the developed AMs was investigated as per our previous method[4] by using the digital refractometer (Mettler Toledo RE40D refractometer) and obtained by the eq.

$$P_m \quad = \quad \frac{1}{A}\,\frac{C_{B(t)}}{C_A\left(t - t_0\right)}\,V_B\,l \qquad (6)$$

where A is the effective membrane area, l the membrane thickness, $C_{B(t)}$ the methanol concentration in compartment B at time t, $C_A(t - t_0)$ the change in the methanol concentration in compartment A between time 0 and t, and V_B the volume of compartment B. All experiments were carried out at 60°C temperature and the uncertainty of the measurements was less than 2%. To assess the suitability of membrane for ADMFCs, we estimated the selectivity parameter (SP) by following relationship.

$$SP(S\,s/cm^3) = \frac{\sigma}{P_m} \qquad (7)$$

where P_m and σ is the methanol permeability (cm^2. s), and hydroxide conductivity ($S.cm^{-1}$) respectively.

References

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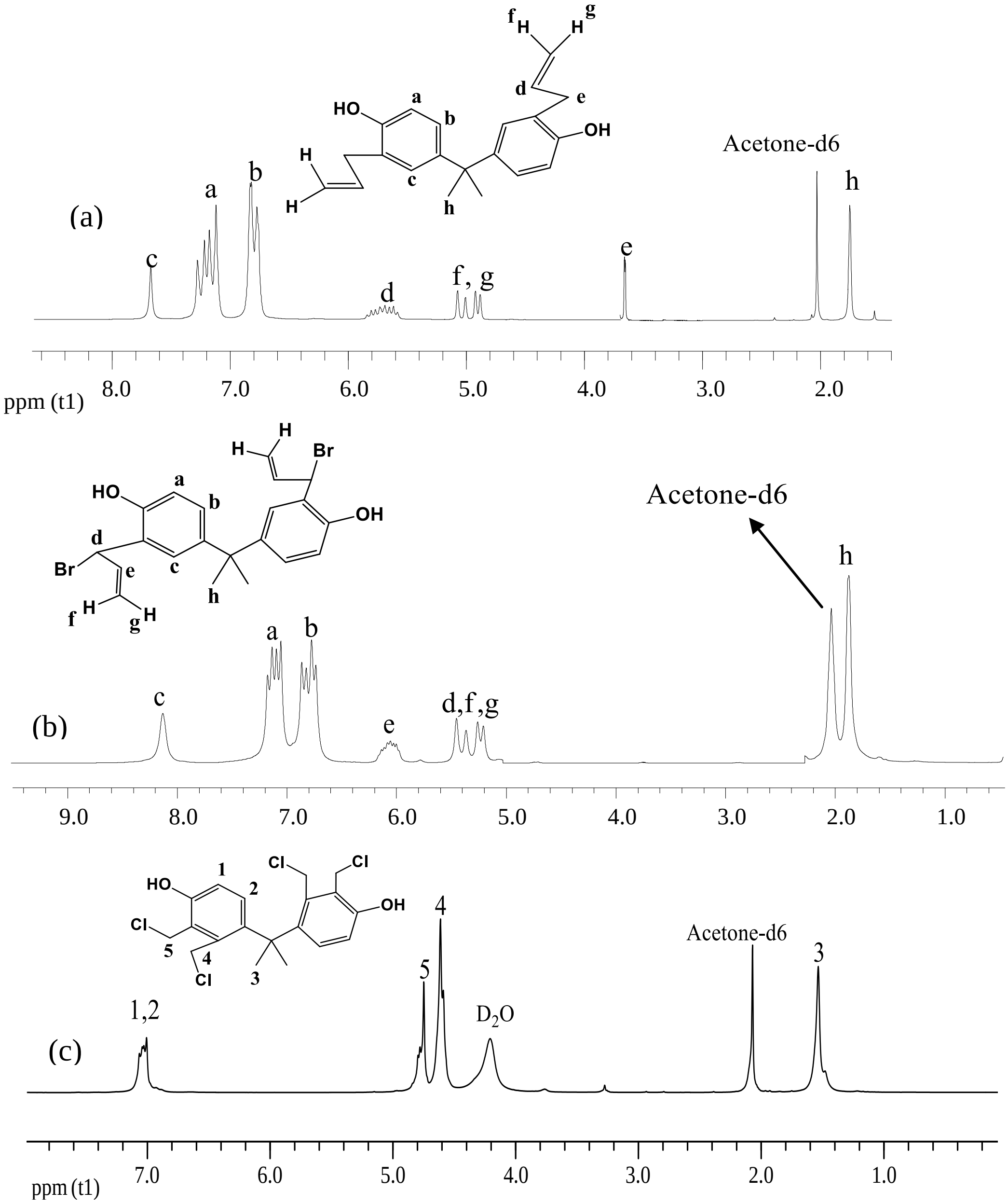

Figure S1. ^{1}H NMR spectra for: (a) ABP, (b) ABP-Br and (C) TCMBP (90% DCM).

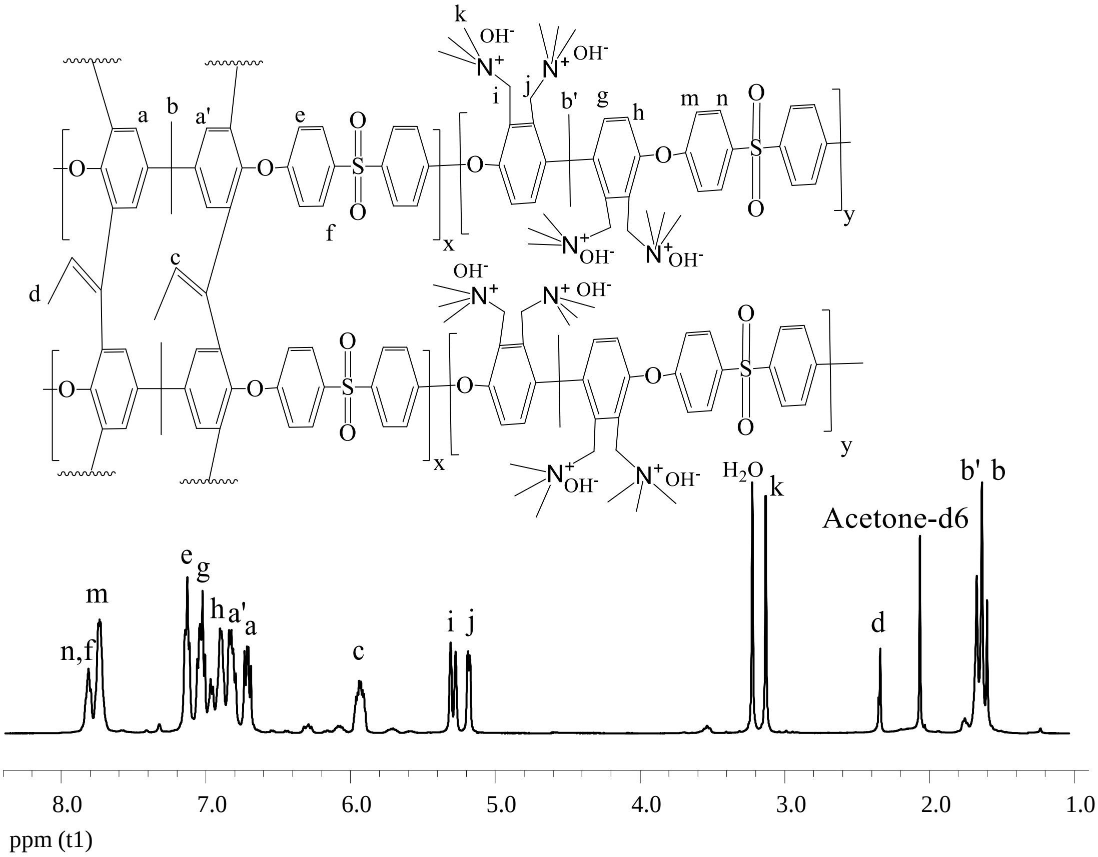

Figure S2. ^{1}H NMR spectra for SCL-ACI (IEC-2.45 meq/g).

Table S1. Reaction conditions for various degree of chloromethylated TCMBP monomers.

DCMs (%)	Formaldehyde (mol)	Thionyl chloride (mol)
35	0.74	0.12
55	1.11	0.18
90	1.60	0.25

Table S2. Comparison study of hydroxide conductivity with other crosslinked ACIs

ACIs	σ /mS cm^{-1}	References
SPES-2OH[a]	18.8 (20 °C)	1
SCL-TPQAOH-0.67[b]	11.5 (20 °C)	2
QAPVA[c]	2.76-7.34 (30 °C)	3
xTQAPS[d]	15.0 (20 °C)	4
SCL-TPQPOH[e]	38 (20 °C)	5
GA-PVA/chitosan-QAOH[f]	2.7–5.3 (25 °C)	6
SCL-ACI-90	68 (30°C)	This work

[a] *Poly(ether sulfone) based on diallyl bisphenol S*
[b] *Self crosslinked trimethyl poly (ether sulfone)-methylene quaternary ammonium hydroxide*
[c] *Cross-linked quaternized poly(vinyl alcohol) (QAPVA)*
[d] *Cross linked tertiary quaternary ammonium poly sulfone*
[e] *Self-crosslinked tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium hydroxide*
[f] *quaternized poly(vinyl alcohol)/chitosan composite*

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Table S3. Loss in ion-exchange capacity (IEC) and hydroxide conductivity (σ) for developed ACIs after alkaline treatment in 6M NaOH at 60 ^{o}C for 300 h.

Membrane	Alkaline stability (%)	
	IEC_{loss}^{*}	σ_{loss}
SCL-ACI-90	9.88	9.96
SCL-ACI-55	6.40	7.63
SCL-ACI-35	4.76	5.72

* *by titration method*

Table S4. Mechanical properties of developed SCL-ACIs.

Ionomers	Young's modulus (GPa)	Elongation at break (%)
SCL-ACI-90	0.44	7.65
SCL-ACI-55	0.72	11.3
SCL-ACI-35	0.97	14.6