



# Quaternized poly (styrene-co-vinylbenzyl chloride) anion exchange membranes for alkaline water electrolyzers



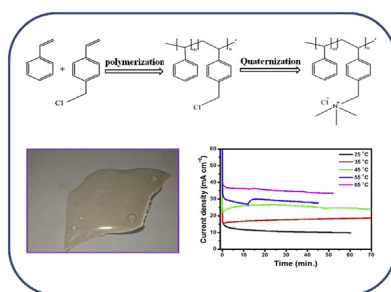
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## HIGHLIGHTS

- Quaternized anion exchange membranes are prepared via chloromethylation free route.
- Styrene to VBC ratio plays a vital role in IC, IEC and water uptake of membrane.
- Membrane with optimum VBC content shows better mechanical properties.
- MEA using the optimized membrane demonstrate a stable performance in electrolyser.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, poly (ST-co-VBC) based anion exchange membranes with different styrene to VBC ratios (1: 0.16, 1: 0.33 and 1: 1) have been prepared via chloromethylation-free synthetic route using aromatic vinyl monomers. The synthesized co-polymers are identified by FTIR and <sup>1</sup>H-NMR analysis. Hydroxide (OH<sup>-</sup>) ion conductivity of the anion exchange membrane with styrene to VBC ratio of 1: 0.33 is as high as  $6.8 \times 10^{-3} \text{ S cm}^{-1}$  in de-ionised water at 25 °C. The membrane also acquires the ion-exchange capacity of 2.14 meq. g<sup>-1</sup>, and the water uptake of 127%. Membrane-electrode-assembly (MEA) using the anion exchange membrane and Ni – foam catalyst demonstrate the current density of 40 mA cm<sup>-2</sup> at 2.3 V in a water electrolyser cell.

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## 1. Introduction

Hydrogen energy is forecasted as one of the prominent energy vectors in 21st century [1,2]. ‘Hydrogen’ is considered as a compact, zero-emission fuel with greater flexibility and overall efficiency. Hydrogen can be produced from abundant domestic resources including natural gas, coal, biomass and plentiful of water [3]. Advanced water electrolysis is the most efficient and economical

way to obtain high purity hydrogen (>99.999%), since it doesn't produce any greenhouse gases as by-products [4]. A number of water electrolysis processes such as alkaline water electrolysis, proton exchange membrane (PEM) electrolysis and steam electrolysis have been developed for the production of hydrogen [5–9]. Of these, alkaline water electrolysis is more preferred, because of the controlled corrosion and cheaper construction materials used [10]. KOH solution is traditionally used as the electrolyte in alkaline water electrolysis. However, electrolyte and electrode degradation caused by the formation of carbonate/bicarbonate in the liquid electrolyte upon reaction of OH<sup>-</sup> ions with CO<sub>2</sub> contamination is one of the major issues associated with alkaline systems [11]. To

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overcome such problems, researches have been more focussed on developing ion-conducting solid polymer membranes. In general, thin polymer membrane can reduce the inter-electrode distance in electro-chemical cells and enhance the system efficiency.

Acidic proton exchange membranes (PEMs) such as Nafion<sup>®</sup> are the most competent among various membrane materials due to their excellent thermal, chemical and mechanical stability. Unfortunately, PEM based membranes impose some drawbacks such as high cost, complicated synthesis and processing, and the necessity of using noble metal catalysts [12]. As an alternative to PEMs, alkaline anion exchange membranes (AAEMs) are considered to be the suitable candidate materials that require non-noble metal catalysts [13–15]. AAEM based systems have drawn greater attention due to several outstanding advantages over PEM systems including faster electro-chemical kinetics, use of non-noble metals and low cost membranes [16]. Basically, AAEM based systems encompass both the benefits of liquid alkaline and PEM systems.

AAEMs are OH<sup>-</sup> ion conductive solid polymer electrolyte membranes which mostly contain quaternary ammonium (QA) groups grafted into the polymer chains. Several quaternary ammonium functionalized polymers such as poly (arylene ether sulfone), poly (phenylene oxide), poly (ether sulfone ketone) and poly (vinyl alcohol) have been developed and used as AAEM materials [17–20]. A key challenge in developing AAEM is to enhance the stability of cationic groups attached to the polymeric backbone. It has been well demonstrated that quaternary ammonium cations are generally sensitive towards  $\beta$ -hydrogen (Hofmann or E<sub>2</sub>) elimination and/or direct nucleophilic substitution (S<sub>N</sub>2) under alkaline conditions [21,22]. The chemical and thermal stability of membrane strongly depends on the nature of QA groups and the polymeric backbone [23,24]. In general, AAEMs are conventionally prepared through chloromethylation of aromatic polymers and subsequent quaternization, alkali-exchange processes [19,25,26]. However, chloromethylation reaction engages chloromethyl methyl ether (CMME) or chloromethyl ethyl ether (CMEE) reagents which are powerful carcinogens; harmful to human health. A safer alternative method to prepare anion exchange polymers is through the polymerization of chloromethylated vinyl monomers [27,28]. Since the vinyl monomer contain chloromethyl groups in its structure, the excess and harmful chloromethylation step can be avoided in the above method. To be highlighted, Luo et al. reported the preparation of series of poly (methyl methacrylate-co-butylacrylate-co-vinylbenzyl chloride) based AAEMs and their application in fuel cells [29–32].

In this work, novel anion exchange membrane is prepared using Styrene-co-Vinyl benzyl chloride (ST-co-VBC) co-polymer as polymer backbone. The co-polymer is prepared via free radical polymerization using styrene, vinylbenzyl chloride monomers and AIBN as an initiator. Further, the co-polymer is quaternized and membrane fabricated by solution casting method. The quaternized anion exchange membrane synthesis route is illustrated in Fig. 1.

The membrane-electrode-assembly (MEA) fabricated using poly (ST-co-VBC) based AAEM and Ni-foam catalyst is tested in water electrolyser for hydrogen production. The membrane characteristics are evaluated in terms of structural analysis, elemental analysis, thermal analysis, morphological analysis, ionic conductivity and ion-exchange capacity measurements.

## 2. Experimental

### 2.1. Materials

Styrene from Sigma–Aldrich (purity > 99%), and vinylbenzyl chloride (VBC) from Acros Organics (purity > 99%) were purchased and used as the monomers; 2, 2'-azobisisobutyronitrile (AIBN)

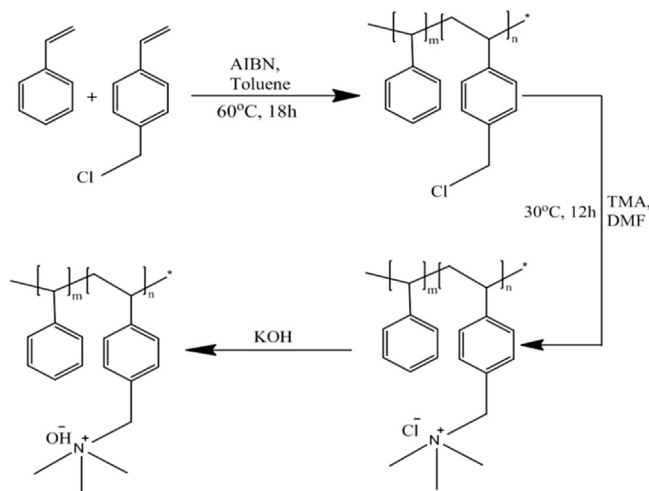


Fig. 1. Synthesis scheme of quaternized poly (ST-co-VBC) anion exchange membrane.

purchased from Sigma–Aldrich was used as initiator. Trimethylamine (TMA), 30% solution was purchased from Agros organics and used as amination agent. Potassium hydroxide (KOH) purchased from Qualigens chemicals, and solvents such as N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), toluene, methanol and chloroform were analytical grade and used as-received. De-ionised water was used throughout the study.

### 2.2. Synthesis of poly (ST-co-VBC) co-polymer and amination

Poly (ST-co-VBC) co-polymer was synthesised via free radical polymerisation [33] and [34]. Briefly, the procedure is as follows: vinylbenzyl chloride and styrene was dissolved in toluene and taken in a 250 mL round bottom flask. Nitrogen gas was purged through the solution for 30 min, and AIBN was added into the solution under N<sub>2</sub> atmosphere. The polymerisation reaction was carried out at 60 °C for 18 h. Then, the solution was cooled and precipitated in methanol. The precipitated polymer was dissolved in chloroform and re-precipitated in methanol. The purification procedure was repeated twice, and the precipitate was dried under vacuum to yield poly (ST-co-VBC). Three different types of co-polymers were synthesized by varying styrene to VBC molar ratios, i.e. 1:0.16, 1:0.33, 1:1, and the corresponding co-polymers were denoted as SV – 0.16, SV – 0.33 and SV – 1, respectively.

For the preparation of quaternized polymer, the synthesized poly (ST-co-VBC) co-polymer was dissolved in DMF and TMA solution was added. The mixture was stirred for 12 h at ambient temperature to obtain the quaternized polymer as a viscous gel. Using the above procedure, three different quaternized polymers were prepared from SV – 0.16, SV – 0.33, SV – 1 co-polymers and denoted as QSV – 0.16, QSV – 0.33 and QSV – 1, respectively.

### 2.3. Membrane preparation

The quaternized co-polymer was dissolved in NMP solvent and stirred at 60 °C for 1 h to obtain homogeneous solution. Then, the viscous solution was casted on a glass plate using doctor blade and dried at 70 °C for 1 h, and further cured at 120 °C for 12 h. Three different types of membranes were prepared using the quaternized polymers QSV – 0.16, QSV – 0.33, QSV – 1, and the membranes denoted as QMSV – 0.16, QMSV – 0.33 and QMSV – 1, respectively. The prepared membrane was peeled-off from the glass plate and soaked in de-ionised water. It was then immersed in 0.5 M KOH

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