



# Effects of metal alkoxides on electro-assisted water dissociation across bipolar membranes

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## ABSTRACT

A bipolar membrane (BPM) was prepared by the layer-by-layer solution casting method (in the same solvent to achieve good adhesion between the layers). Thin films of different metal alkoxides ( $M(OR)_n$ , where M is Si, Ti or Zr, and R is  $-(CH_2)_n-CH_3$ ) were used as interfacial layers (ILs), which were sandwiched between heterogeneous anion-exchange layers (AELs) and homogeneous cation-exchange layers (CELs) of sulfonated poly (ether sulfone) (SPS). The CELs and the AELs were separately evaluated for their physicochemical and electrochemical properties. BPMs prepared with ILs (containing different metal alkoxides) showed good stability and low resistance. Current–voltage ( $i$ – $V$ ) curves were explained in terms of the first limiting current density ( $i_{lim1}$ ), the second limiting current density ( $i_{lim2}$ ), the water dissociation potential ( $V_{diss}$ ), the water dissociation resistance ( $R_{diss}$ ) and the operational area resistance ( $R_{op}$ ). The catalytic activity of the metal alkoxides improved the water dissociation performance of the BPMs. The BPM–SiOH performed better than the commercially available BPMs. Furthermore, electrolysis with a bipolar membrane (EDBPM) experiments confirmed that water dissociation occurred at the BPM interface and thus acid and base formation occurred.

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## 1. Introduction

Bipolar membrane (BPM) is a laminate of an AEL and a CEL with suitable IL that allows the dissociation of water into  $H^+$  and  $OH^-$  under the influence of an electric field [1]. Three layers of a BPM play important role in its performance during electrolysis. EDBPM is a small chemical reactor that integrates the dissociation and separation of water. It offers the possibility of producing an acid and a base from their corresponding salts and solves other industrial problems related to separation [2–8]. To improve the performance of a BPM for water dissociation, a thin IL is generally introduced between the CEL and the AEL [9].

Water dissociation catalysts include organic compounds containing functional groups, polyelectrolyte complexes (poly(4-vinylpyridine) and poly(acrylic acid)), heavy metal ion complexes of ruthenium trichloride, chromic nitrate, indium sulfate, and metal oxides [10–14]. Metal alkoxides, which are hydrophilic in nature, showed different types of hydrolysis under acidic and basic conditions. The resulting hydrolysis products further established hydrogen bonding/polar interactions with the anionic and cationic

layers. The interaction between the metallic residues and the membrane surface plays an important role in the enhancement of water dissociation [15]. Several researchers have suggested mechanisms for enhanced water dissociation due to the presence of metal alkoxides in the IL [11,16,10,17]. Sheldeshov et al. studied the rate of water dissociation using a cation-exchange membrane with a thin layer of water insoluble metal hydroxides ( $Cu(OH)_2$ ,  $Fe(OH)_3$ ,  $Co(OH)_2$ , and  $Ni(OH)_2$ ) [15,16]. The thin layer of metallic compounds at the interface decreased the water dissociation potential by enhancing the hydrophilic and conductive nature of the surface for  $H^+$  and  $OH^-$  [11,18]. Zabolotskii et al. observed the formation of metal complexes, which lead to catalytic water dissociation [15,19]. However, many aspects of the water dissociation mechanism induced by metal alkoxides and their effect on their hydrophilic nature have still not been studied in a systematic manner.

In this manuscript, the effect of metal alkoxides (present in the IL of a BPM) on the rate of water dissociation was studied. BPMs were prepared by the layer-by-layer casting method in the same solvent (dimethylacetamide) for better compatibility with the IL of the different metal alkoxides (tetraethylorthosilicate, zirconium (IV) propoxide and titanium (IV) butoxide). The silicon alkoxide was considered to be efficient for the dissociation of water, and the feasibility of its application as a novel water dissociation catalyst was investigated.

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## 2. Experimental

### 2.1. Materials

The anion-exchange resin (INDION FFIP), a chloromethylated and aminated polystyrene (with an 8% cross-linking density and a 3.4 mequiv./g ion-exchange capacity), was supplied by Ion Exchange (India) Ltd. Poly(ether sulfone) (PES) (Udel P-3500) was received from Solvay Advanced Polymers and tetraethoxysilane, titanium (IV) butoxide and zirconium (IV) propoxide were received from Sigma–Aldrich Chemicals and used without any purification. All other reagents, such as dimethylacetamide (DMAC), sodium chloride (NaCl), methanol (MeOH), hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) of AR grade, were obtained from S.D. Fine Chemicals, India; these chemicals were also used without further purification.

### 2.2. Preparation of monopolar and bipolar membranes

The anion-exchange resin was dried (60 °C for 24 h), powdered in a ball mill and sieved (100 mesh sizes) before being dispersed in a PES solution in DMAC (60% (w/v) and total solid:DMAC ratio of 1:5, w/v). The AEL was then cast onto a clean glass plate at ambient temperature and was allowed to dry at 60 °C for 24 h. The AEL was swollen in a mixture of 5:1 (v/v) MeOH:H<sub>2</sub>O at 25 °C for 24 h to allow water and metal alkoxides to penetrate the membrane. Metal alkoxides (M(OR)<sub>n</sub>, where M is Si, Ti or Zr, and R is  $-(CH_2)_n-CH_3$ ) were prepared by the sol–gel process in a methanol–water mixture (5:1, v/v) under acidic (HCl) conditions [20]. To prepare the IL, the resulting gel was transformed into a thin film (10 μm) on top of the AEL and dried under IR lamps for 4 h. SPS was prepared by sulfonation of PES as described previously [21], and a solution of SPS was prepared in DMAC (15%, w/v). A CEL of desired thickness was then cast onto the composite AEL-IL structure to obtain the BPM and dried at room temperature under IR lamps for 12 h. To achieve good contact between the different layers, the casting method reported previously was used [5]. After the solidification of the first layer, the next layer was cast onto the top surface of the previous one and was allowed to dry. Polymer solutions were prepared in the same solvent, to achieve good contact between different layers. An AEL and a CEL of 150 μm thicknesses each were prepared separately and used as an AEM and a CEM in this investigation. The prepared BPMs were dried in an inert atmosphere at 40–80 °C for 24 h and then immersed in water. Membranes obtained in this manner were equilibrated by treatment with 1.0 M NaOH and 1.0 M HCl and finally stored in a 1.0 M NaCl solution. BPMs prepared in this manner were designated as BPM–MOHs, where M was the metal (Si, Ti or Zr) used for the preparation of the interfacial layer.

### 2.3. Instrumental analysis

FTIR spectra for membranes were recorded by the ATR technique with a Spectrum GX Series 49387 spectrometer in the range of 4000–600 cm<sup>-1</sup> (section S1; supporting information). The surface and cross-sectional morphologies of dried membranes were observed with a scanning electron microscope (SEM) (LEO Instruments (H.K.) Ltd., Kowloon, Hong Kong) after gold sputter coatings were applied to the desired samples. The chemical compositions of the BPMs were determined by energy dispersive X-ray analysis (EDX) (section S2; supporting information).

### 2.4. Physicochemical characterizations

The detailed procedures for the determination of the water content ( $\varphi_w$ ), the ion-exchange capacity (IEC) and the concentration of the ion-exchange group ( $\chi^m$ ) are included in the (section S3;

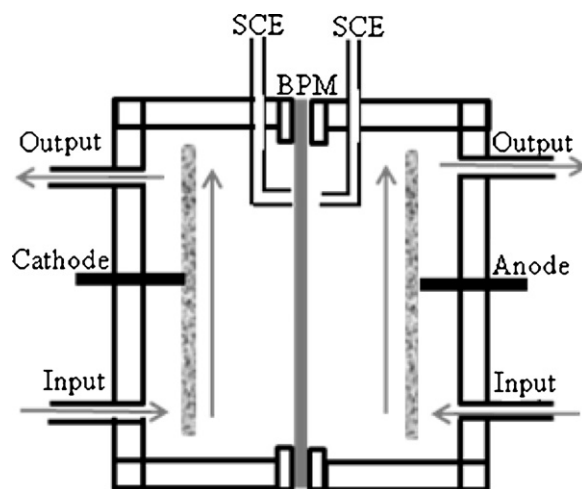


Fig. 1. Cell used for *i*–*V* curve characteristics and chronopotentiometry.

supporting information). A membrane chronopotentiometry study was used to estimate the permselectivity of the CEL and the AEL (section S4; supporting information). Membrane resistance ( $R^m$ ) measurements for the AEL, the CEL and the BPMs in equilibrium with a 0.5 M NaCl solution were carried out with an Autolab Model PGSTAT 30 potentiostat/galvanostat frequency response analyzer (Eco Chemie, Utrecht, The Netherlands) (section S5; supporting information) [22].

Current–voltage polarization (*i*–*V*) curves of the BPMs (with different ILs) in equilibration with a NaCl solution (2.0 M) were recorded in a two-compartment cell with a four-electrode arrangement (Fig. 1) [23]. Compartments (500 cm<sup>3</sup>) that were filled with a constantly stirred electrolyte solution were separated by the BPM. A constant current was applied across the BPM using a Model L1285 DC power supply (Aplab Ltd., India) and precious triple metal oxide (titanium–ruthenium–platinum (6.0 μm thickness))–coated Ti sheet electrodes were fixed in both chambers. The resulting potential difference across the membrane was measured with saturated calomel electrodes and a digital multimeter (Systronics (India) Limited, India).

### 2.5. EDBPM experiments for the determination of water dissociation efficiencies

To study the water dissociation efficiency of different BPMs, EDBPM experiments were carried out with NaCl solutions in a four-compartment (catholyte, anolyte, comp. 1, and comp. 2) electro-dialysis cell containing a BPM, a CEM and an AEM (Fig. 2). A separate flow arrangement was used for each compartment. Peristaltic pumps were used to feed the respective compartments

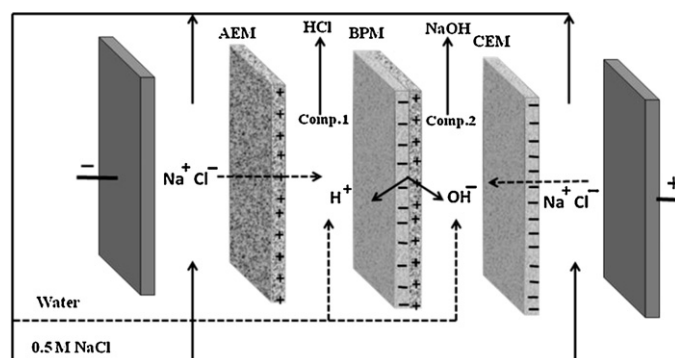


Fig. 2. Schematic diagram of an EDBPM cell.

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