# A novel approach for stable anion exchange membrane: Self-assembled multilayer formation on the membrane via LbL method

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ABSTRACT

In this study, KOH doped poly (vinyl alcohol)(PVA) membranes with improved and stable ionic conductivity were successfully synthesized by Layer-by-Layer (LbL) method. For the formation of multilayer structure on the membrane surface by LbL method, poly(diallyldimethylammonium chloride) (PDDA) as polycation and polystyrene sulfonic acid sodium salt (PSS) as polyanion were used. In order to explore the effect of cross-linker type on anion exchange membrane, two series of KOH doped PVA membranes were prepared by cross-linking with glutaraldehyde (GA) or poly(ethylene glycol)diglycidyl ether (PEDGE). The membranes were characterized in detail by infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), contact angle, water uptake, swelling ratio, ionic conductivity, long term stability and quartz crystal microbalance-dissipation (QCM-D) to evaluate their applicability in anion exchange membrane fuel cell (AEMFC). PVA membranes cross-linked with PEDGE exhibit a slight decay in ionic conductivity during long term stability test and higher conductivity than that of membranes cross-linked with GA. The ionic conductivity of the membranes were observed to be increased with the number of bilayers and reached $2.28 \, \text{mS cm}^{-1}$ for PPP-20L membrane. Also, the loss percent in ionic conductivity regressed to 25% at the end of 15 days. QCM-D studies revealed that the multilayered film was stable against fuel cell operating conditions in terms of pH. These results indicate that the formation of multilayered ultrathin film on the AEM by LbL technique is promising to develop KOH doped-AEMs having high stability and ionic conductivity for fuel cell applications.

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## 1. Introduction

In the past decade, there has been a tremendous effort to develop an alternative renewable power sources and energy conversion systems. Most of the research was focused on fuel cell technology due to their high efficiency and low pollution level. Although proton exchange membrane fuel cells (PEMFC) exhibiting chemical, mechanical, thermal stability and high ionic conductivity have been developed to date, their commercialization has been hampered by low durability and high cost of membrane and catalyst [1]. The slow kinetic of oxygen reduction reactions in acidic media requires the use of noble metal catalyst (Pt). Nafion® is commercially available membrane for PEMFC technologies, but its high cost and difficulties in synthesis restrict its usage. Unless PEMFCs are produced in cost effective, it is difficult to be competitive with traditional power sources. On the other hand, anion exchange membrane fuel cells (AEMFC) have significant advantages over PEMFCs in terms of cost. Due to the faster electrode kinetics in the alkaline medium compared with an acidic medium [2], AEMFCs allow the use of a smaller amount of noble metal catalyst or non-precious metal catalyst. In addition, the water management and the fuel crossover problem are improved owing to the opposite direction of ion transport in the membrane. Thus, AEMFCs have begun to attract considerable attention in the last few years [3].

The transport of hydroxide anions through anion exchange membrane (AEM) occurs via hydroxide salt or cationic group in the membrane structure. If the AEM consists of a hydroxide salt and a water-soluble polymer, the membrane is called ion-solvating polymer. Ionic conduction within this structure is based on the interaction between electronegative heteroatom in the polymer chain and cation of the salt [4]. For AEMFC applications, the main challenges about the ion-solvating polymer membrane are unstable conductivity and thus unstable performance. KOH as a hydroxide salt is very soluble in water and the ionic conductivity of AEM tightly depend on the amount of KOH in the membrane. Therefore, the leakage of KOH from the matrix with time causes power loss in AEMFC [5]. Some approaches have been tried to trap

KOH inside the membrane. Fu et al. [6] synthesized AEMs based on KOH doped PVA which was chemically cross-linked by glutaraldehyde. Ionic conductivity of this cross-linked PVA membrane depending on the concentration and temperature of KOH solution was discussed in detail. They reported that the ionic conductivity increased with increasing of KOH concentration and immersion temperature. On the other hand, Merle et al. [7] investigated the effect of cross-linking agent type. By using poly(ethylene glycol) diglycidyl ether (PEDGE) as a cross-linker, they developed membranes exhibiting high long term ionic conductivity and good chemical stability. In another study, Qiao et al. [8] prepared AEMs by blending PVA and PVP (poly(vinylpyrrolidone)). They reported that the addition of PVP into the PVA matrix allowed the excess KOH to remain in the membrane.

Some studies are available about the liquid fuel cross-over properties of the LbL self-assembled composite membranes in fuel cell applications. These studies have indicated that the formation of ultrathin film on the membrane surface by LbL method prevents the fuel permeation through the membrane. Deligöz and co-workers reported that Nafion 117 membrane was deposited by polyallylamine hydrochlorid (PAH) and polystyrene sulfonicacid sodium salt (PSS) and observed that the self-assembled multilayered film on Nafion membrane suppressed the methanol permeability of the membrane [9]. In another study, they was observed that the addition of salt to the polyelectrolyte solution used for preparing LbL self-assembled membrane improved both ionic conductivity and methanol blocking [10].

Up to our best knowledge, the use of an ultrathin barrier film on anion exchange membrane surface for blocking KOH leakage hasn't been investigated and reported yet. In this study, we attempted to prepare multilayered PVA membranes by Layer-by-Layer method to hold KOH inside the membrane. Based on this consideration, firstly, AEMs based on PVA/PDDA (poly(diallyldimethylammonium chloride)) were prepared by cross-linking with glutaraldehyde (GA) or poly(ethylene glycol) diglycidyl ether (PEDGE). Secondly, the deposition of self-assembled polyelectrolyte multilayer on AEM carried out by LbL technique. PDDA was especially chosen as a cationic polyelectrolyte because it bears a quaternary ammonium group, which can serve as anion conductor as well as KOH. The results showed that the developed membranes exhibited not only high conductivity but also improved long term stability.

## 2. Experimental

### 2.1. Materials

Poly(vinyl alcohol)(PVA) (99% hydrolyzed, $M_w = 89{,}000$-$124{,}000$), Poly(ethylene glycol) diglycidyl ether (PEDGE) ($Mn = 526 \, g \, mol^{-1}$), Polystyrene sulfonic acid sodium salt (PSS) ($M_w = 70\,000$), glutaraldehyde (GA) (25 wt.% in water) were purchased from Aldrich. Poly (diallyldimethylammonium chloride) (PDDA) ($M_w = 240\,000$) was supplied from Polyscience. Hydrochloric acid (HCl) (37 wt.%) and aceton were purchased from Riedel de Haen. All the chemicals were used without further purification.

### 2.2. Membrane preparation

The PVA-based membranes were prepared by solution casting method. PVA solution (5 wt.%) was prepared by dissolving PVA in deionized water at 90° C for 2 h under stirring. The solution was cooled down to room temperature and 10 wt.% PDDA was added under stirring in blend ratio: PVA:PDDA being 1:0.5 in mass. The homogeneous solution was cast onto petri dishes and dried at 40° C for 2 days. For the cross-linking reaction with GA, the dry membrane was immersed in a reaction solution consisting of 10 wt.% GA in aceton and HCl as catalyst. For the crosslinking with

PEDGE, PEDGE was added dropwise to the homogeneous PVA/PDDA solution, in which the PVA/PEDGE was 1:1 by mass. The prepared membranes were named as PPG and PPP, respectively. All membranes were immersed in 4 M KOH for 24 h solution in order to prepare KOH doped AEMs. Prior to application of LbL technique on the surface of the membrane, the membranes were washed with deionized water several times to remove KOH on its surface. The thickness of the membranes was between 80 and 140 μm.

Polyelectrolyte complex coated-membranes were prepared by Layer-by-Layer technique (LbL) according to the previously reported study [9]. The LbL self-assembly of PDDA–PSS was carried out by alternate dipping of the PPG or PPP membrane into anionic and cationic polyelectrolyte solutions. Polyelectrolyte solutions were prepared at $10^{-2}$ monomol concentration. pH of the polyelectrolyte solutions was adjusted to 5.5. After each dipping step, the membrane was rinsed with Mili Q water to remove weakly bonded polyelectrolyte molecules. This process was repeated 5, 10 or 20 times to increase the number of bi-layers on PVA-based membrane. For example, five deposited bi-layers of PDDA/PSS was denoted as PPG–5 L or PPP-5L. The membranes were labeled according to cross-linker agent types and the number of bi-layers. The details are shown in Table 1.

### 2.3. Characterization

The chemical structures of AEMs were determined by Fourier transform infrared spectroscopy (FTIR) with a Perkin Elmer Spectrum One FTIR with attenuated total reflectance (ATR) unit and the membranes were scanned between the wave number of 600 and 4000 $cm^{-1}$.

X-ray diffraction (XRD) patterns of the membranes were measured to characterize the crystalline state of the AEMs using a Rigaku D/Max 2200/PC X-ray diffractometer with Cu Kα radiation.

Thermal analysis of the membranes were performed using a Seiko EXSTAR 6000-TGA/DTA 6300 model instrument with a heating rate of 10 °C min$^{-1}$ under a nitrogen atmosphere the temperature range of 30–700 °C.

Contact angle measurements of the membranes were performed using KSV Attension Tensiometer. The contact angles presented here are static contact angles measured with the standard pendant drop technique and volume of the water droplet was maintained constant at 5 μL.

The water uptake (WU) of the AEMs were determined from the mass change before and after immersion in deionized water at ambient temperature. The samples were dried and weight, then, immersed in water for a day. After removal of surface attached water, membranes were weighed again. The WU value was

**Table 1**
Designation of AEMs –based on PVA.

| Membrane | Cross-linker | The number of deposited bi-layers |
| --- | --- | --- |
| PVA-GA[a] | GA | – |
| PPG | GA | – |
| PPG-5L | GA | 5 |
| PPG-10L | GA | 10 |
| PPG-20L | GA | 20 |
| PVA-PEDGE[b] | PEDGE | – |
| PPP | PEDGE | – |
| PPP-5L | PEDGE | 5 |
| PPP-10L | PEDGE | 10 |
| PPP-20L | PEDGE | 20 |

[a] PVA-GA: PVA cross-linked with GA.
[b] PVA-PEDGE:PVA cross-linked with PEDGE.