

# Synthesis of Chloride free Potash Fertilized by ionic Metathesis using Four Compartment Electro-dialysis Salt Engineering

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## S-1 Synthesis of membranes

Bromination of PPO is carried out by the nucleophilic substitution reaction as describe earlier. Briefly, 12 gm (100 mmol) of PPO is dissolved in the chlorobenzene with a continuous stirring, 8.9 gm (50 mmol) of N-bromosuccinamide (NBS) and 0.5 gm of 2, 2'-azobis-isobutyronitrile (AIBN) as an initiator is added to this solution. The reaction mixture is kept on a hot plate at 135° C temperature for 3 hours with stirring condition. After completion of reaction the solution is cooled down to the room temperature and precipitated into 10 fold of ethanol. The precipitate is dried and dissolved in chloroform; again the solution is precipitated into the ethanol to get light yellow in color product. The functionalization of Br-PPO with 1-vinylimidazole is performed using following procedure. 4 gm of Br-PPO is dissolved in NMP in a three neck flask, after complete dissolution 1 gm of catalyzed 1-vinylimidazole (CVI), is added into the reaction mixture dropwise at room temperature under the nitrogen atmosphere. After completion of the reaction the solution is cooled down and poured on a clean glass plate and spread it with doctor's knife to have desired thickness and kept at 60°C for overnight. For converting the film in to anion conducting membrane the dry films are further treated with triethylamine (TEA) 33% aqueous solution for the 12 hours under the room temperature to ensure the complete conversion of -CH<sub>2</sub>Br group into the subsequent quaternized amine group. Now the membrane are taken out and washed with deionized water and further dipped into the 1 M NaOH to convert it in its hydroxyl form, finally membranes are washed with deionized water carefully to complete removal of NaOH.

Sulfonated polyether sulfone based cation exchange membranes are used for the study as reference. Sulfonation of polyethersulfone is carried out as reported earlier using conc. H<sub>2</sub>SO<sub>4</sub>

(95–98%). Functionalized polyethersulfone dissolved in DMAC and the resulting solution was cast on glass followed by vacuum drying. The membranes are conditioned by treatment with 0.1 M HCl and 0.1 M NaOH successively and then thoroughly washed with distilled water before use.

### ***S-2 Chemical, thermal and mechanical characterization of CEM and AEM***

Synthesized CEMs and AEMs were characterized for their chemical, thermal and mechanical behavior by the means of FTIR, thermogravimetric analysis (TGA) and universal testing machine (UTM) respectively. The Fourier-transform infrared (FTIR) spectra of membranes is recorded using KBr pellet method with a spectrum GX series 49387 spectrometer in the frequency range 4000-400 cm<sup>-1</sup>. Thermal properties of CEMs and AEMs were investigated by thermogravimetric analyser (TGA) under N<sub>2</sub> atmosphere on Mettler Toledo TGA/SDTA851e with stare software, with a heating rate of 10 °C/min from 30° to 600°C. Stress-strain property of membrane samples (2.5 cm long, 0.5 cm width and 0.15 mm thick) is determined using Zwick Roell Z2.5 tester. The test Xpert II -V3.5 software was used for data analysis. Measurements are carried out with 3 samples, whose average is reported in dry as well as in wet condition.

### ***S-3 Physicochemical characterization of CEM and AEM***

To evaluate the performance of synthesized CEMs and AEMs in MED processes, membranes were physicochemically characterized with their ion exchange capacity (IEC), ionic conductivity (IC), water uptake, number of water molecules per ionic site ( $\lambda$ ) and dimensional stability.

Water uptake behaviors of prepared membranes were determined by recording the dry and wet weight. Membrane samples of 2×2 cm<sup>2</sup> were dipped in DI water for 24 h; subsequently membrane samples were weighted after wiping surface. Dry weight of sample were also calculated on vacuum drying at 100°C for 2h. Water uptake ( $\varnothing_w$ ) for membranes was calculated by using the following formula:

$$\varnothing_w = \frac{W_{wet} - W_{Dry}}{W_{Dry}} \times 100\% \quad \dots\dots\dots (1)$$

Where  $W_{wet}$  and  $W_{dry}$  are the wet and dry weight of membrane samples.

IEC of membrane samples was calculated using simple acid-base titration for CEMs and classical Mohr's method for AEMs with the following equation:

$$IEC = \frac{V \times C}{Wdry} \dots\dots\dots (2)$$

Ionic conductivity of the membranes was measured in water using potentiostat (CH-608E). Membrane sample of 1 cm<sup>2</sup> is immersed in NaCl (0.1M) for 24 h and then washed with DI water in order to remove excess of NaCl. Membrane sample is sandwiched between two circular steel electrodes (1 cm<sup>2</sup>). Membrane samples resistance was obtained by Nyquist plot, and ionic conductivity ( $\sigma$ ) was calculated from the equation:

$$\sigma (\Omega^{-1} \text{ cm}^{-1}) = \frac{L (\text{cm})}{R(\Omega) \times A(\text{cm}^2)} \dots\dots\dots (3)$$

Where A is the surface area of membrane sample, R is the resistance of membrane sample and L is the distance between the electrodes used to measure the potential.

**S-4 Energy Consumption**

The specific energy consumption ( $P$ ) and current efficiency ( $\eta$ ) for production of potassic fertilizer can be obtained by following equation;

$$P (kWhkg^{-1}) = \frac{1}{m} \int_0^t UI dt \quad (2)$$

$$\eta = \frac{FnV (C_0 - C_t)}{n_c \int_0^t Idt} \times 100 \quad (3)$$

where  $\eta$  is the current efficiency (%),  $F$  is Faraday constant (A.h.mol<sup>-1</sup>),  $V$  is the volume of the dilute (dm<sup>-3</sup>),  $C_0$  and  $C_t$  (mol) are the concentration of dilute compartment at zero time and time  $t$ ,  $n$  is the charge number of the counter ions,  $n_c$  is the number of cell pair,  $U$  is the applied potential (V) and  $I$  is current (A).