



## Research Paper

## *In situ* ion substitution of sodium gluconate: Comparison of bipolar membrane electro dialysis and electro-membrane reactor for producing gluconic acid

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## HIGHLIGHTS

- Home-made CEM and BPM, EDBPM and EMR-3 were developed to recovery of GLH from its sodium salt.
- The production of NaOH as a byproduct is a spinoff of the EMR-3 and EDBPM.

## ARTICLE INFO

## Article history:

Received: 2014-03-28  
Revised: 2014-06-08  
Accepted: 2014-06-16

## Keywords:

Ion substitution  
Ion-exchange membrane  
Bipolar membrane  
Electrodialysis  
Gluconic acid

## ABSTRACT

Based on the home-made cation-exchange membrane (CEM) and bipolar membrane (BPM), electro dialysis with bipolar membrane (EDBPM) and electro-membrane reactor with three compartments (EMR-3) were developed to achieve *in situ* ion substitution and recovery of gluconic acid (GLH) from its sodium salt. Physicochemical and electrochemical properties of CEM and BPM were studied to assess their suitability under standard operating conditions. Results showed that the proposed EMR-3 proved a promising tool for *in situ* ion substitution of GLNa with high current efficiency: CE (93%), and low energy consumption (1.28 kWh/kg of GLH produced). The EMR-3 process performances were dependent on GLNa feed concentration in the central compartment (CC), applied current density and electrochemical properties of CEM/BPM. Furthermore, high CE, recovery of GLH and low energy consumption of EMR-3 in comparison with EDBPM revealed its ion substitution of GLNa. It was concluded that EMR-3 is a more efficient process in comparison with EDBPM for *in situ* ion substitution of GLNa producing GLH. The production of NaOH as a byproduct in the cathode stream is a spinoff of the EMR-3 and EDBPM.

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## 1. Introduction

Gluconic acid (pentahydroxycaproic acid) (GLH) has wide applications in dairy, metallic, textile, food and pharmaceutical industries [1]. Salts of gluconic acid were used in the pharmaceutical industry for calcium deficiency, iron therapy, common cold, wound healing and various diseases such as mental lethargy, skin change etc. [2]. Scheme S1 (supporting information) describes currently conventional processes used for the production of gluconic acid from glucose by fermentation using *Aspergillus niger* [3,4]. Obtained GLNa was converted into GLH by acidification with H<sub>2</sub>SO<sub>4</sub> and yielded Na<sub>2</sub>SO<sub>4</sub>. This process requires excess inorganic acid and distilled water for several successive and salt separations. Thus, it is urgent to investigate an alternative eco-friendly and economically viable process for producing GLH from GLNa without the use of any chemicals or acids.

Many processes for GLH recovery from GLNa without precipitation were studied. Disadvantages of ion exchange, solvent extraction, ED and EDBPM for ion substitution of GLNA are described in Scheme S1 of supporting informations [5-7]. Membrane technology, especially ion-exchange membranes, offers many advantages that align well with the current general trends related to resources and energy management in the world. Electrodialysis (ED) is a promising technique for the separation of organic acids from fermentation broth and enzymatically produced solutions [8-10]. Recent progress enabled the development of EDBPM to convert salt into corresponding acid and base by water splitting. BPM is composed of CEM and anion-exchange membrane (AEM). The H<sup>+</sup> and OH<sup>-</sup> ions, generated by water splitting in the interfacial region of the membrane under the influence of the electric field, migrate towards cathode and anode, respectively [11-15].

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Both ionic layers of BPM allow the selective transport and sufficient water flux to fill the water consumed by its dissociation at the interfacial layer [12]. EDBPM was used to regenerate inorganic/organic acids and bases from their salts, concentration of citric acid, acidification of gluconate into gluconic acid etc. [16-22]. Novalic et al. [23] reported the conversion of GLNa into GLH by EDBPM, containing an ED unit with several cell pairs of CEM, AEM and BPM. In addition, operation cost and salt diffusion through the bipolar membrane is a serious problem that affects the product purity.

Herein, we are reporting a novel EMR-3 for *in situ* ion substitution of GLNa for GLH recovery, based on the principles of electro-electrodialysis. Indigenously prepared CEMs separated the catholyte and anolyte.  $H^+$  formed by oxidative water splitting at the anode migrated towards the central compartment and exchanged with  $Na^+$ . Liberated  $Na^+$  further migrated towards the catholyte through CEM and formed NaOH as a byproduct. Furthermore, process efficiency and energy consumption of EMR-3 for the producing GLH were compared with EDBPM under similar experimental conditions.

## 2. Experimental

### 2.1. Materials and membranes preparation

Poly (ether ether ketone) (PEEK), poly(4-vinyl pyridine) and Poly (ether sulfone) (PES) were received from Sigma-Aldrich Chemicals. All other chemicals such as sodium gluconate (GLNa), gluconic acid (GLH),  $H_2SO_4$ , NaCl,  $Na_2SO_4$ ,  $Cu(SO_4)_2 \cdot 5H_2O$  and dimethyl acetamide (DMAC) etc. of AR grade were obtained from S.D. Fine Chemicals, India. All chemicals were used without any further purification. Anion-exchange resin (Indian FFIP), a chloromethylated and aminated polystyrene (with 8% cross-link density and 3.4 mequiv./g ion-exchange capacity) was supplied by Ion-exchange (India).

#### 2.1.1. Preparation of Anion-exchange membrane (AEM)

For the preparation of heterogeneous AEM, anion-exchange resin particles were dried in an oven at 60 °C for 24 h, powdered in a ball mill and sieved to 100 mesh size. The desired amount of powdered anion-exchange resin was dispersed in PES solution in DMAC (60%, w/v) with total solid: DMAC ratio: 1:5 (w/v), and stirred for 8 h. Dispersion was casted into a thin film onto a clean glass plate at ambient temperature and allowed to dry at 60°C under IR lamp for 24 h.

#### 2.1.2. Preparation of cation-exchange membrane (CEM)

Sulfonation of PES was carried out using conc.  $H_2SO_4$  at 50 °C under stirred conditions [24]. CEM was prepared by dissolving sulfonated poly(ether sulfone) (SPES) in DMAC (20%, w/v), and solution casting onto a clean glass plate. The membrane was allowed to dry under IR lamps for 24 h followed by a vacuum oven for 6 h. Thus, the obtained membranes were equilibrated in 1.0 M HCl and NaOH and washed with distilled water before their practical application. Versatile electro-dialysis applications of this membrane have been developed because of its high ionic conductivity, chemical and mechanical stabilities [25-28].

#### 2.1.3. Preparation of bipolar membrane (BPM)

Sulphonated poly(ether ether ketone) (SPEEK) was prepared by sulphonation of PEEK (450PF), obtained from Victrex as described earlier [24]. Dried SPEEK was dissolved in DMAC (10% w/v) under constant stirring to get the clear solution. The method for the preparation of BPM has been reported earlier [29]. For the contact region of BPM, the poly (4-vinyl pyridine) layer was coated on the surface of a heterogeneous anionic layer (AL), while the SPEEK (degree of sulphonation: 80%) layer was coated on top and dried under IR lamps. Then the cationic layer (CL) of SPEEK solution was casted onto the composite structure to get BPM and dried at room temperature under IR lamp for 12 h. The schematic procedure for the preparation of BPM is presented in the supporting information (Scheme S1). To achieve good contact between the different layers, the casting method was used as reported earlier [29]. The polymer layers were casted with the desired thickness. After the solidification of one layer the next layer was casted onto the top surface of the previous layer, which was then allowed to dry under IR lamp. The contacts between the interfacial layers were firm because all polymer solutions were prepared in the same solvent. The prepared membranes were dried in inert atmosphere at 40–80 °C for 24 h, and then immersed in water. Thus, the obtained membrane was equilibrated by treatment with 1.0 M NaOH and 1.0 M HCl, and finally stored in a 2.0 M NaCl solution.

### 2.2. Membrane properties

Membrane conductivity measurements for CEM, AEM and BPM were carried out after equilibration with NaCl and sodium gluconate solutions of various concentrations using a potentiostat/galvanostat frequency response analyzer (Auto Lab, Model PGSTAT 30). The membranes were sandwiched between two in-house made stainless steel circular electrodes (2.0 cm<sup>2</sup>). The direct current (dc) and sinusoidal alternating currents (ac) were supplied to the respective electrodes for recording the frequency at a scanning rate of 1  $\mu A/s$  within a frequency range of 106 to 10 Hz. Nyquist plots (Schemes S2 and S3; supporting information) were obtained and membrane resistance was determined using the Fit and Simulation method [30].

The thickness of the membranes was measured by a digital micrometer up to 0.10  $\mu m$  accuracy. The membrane water content was determined by the weight difference of the membrane in wet and dry conditions using the following Equation:

$$\text{Water content (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where  $W_w$  and  $W_d$  are the weight of the wet and dry membrane, respectively.

For the estimation of ion-exchange capacity (IEC), the desired pieces of ion-exchange membranes were conditioned in 1.0 M HCl and NaOH solution overnight to convert them into  $H^+$  and  $OH^-$  form. The excess HCl or NaOH was removed by washing with distilled water. The membranes were then equilibrated in 50 ml of 0.50 M NaCl solution. The amount of  $H^+$  or  $OH^-$  ions liberated from CEM and AEM was determined by acid-base titration [31].

The counter-ion transport number ( $t_i^m$ ) across the membranes was estimated by membrane potential measurement in NaCl solutions (0.055 M mean concentration) using the TMS (Teorell, Meyer, and Sievers) approach according to the following expression [31]:

$$E^m = (2t_i^m - 1) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad (2)$$

where  $a_1$  and  $a_2$  are the activities of electrolyte solutions contacting two surfaces of the membrane,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $F$  is Faraday constant.

### 2.3. Experimental procedure for bipolar membrane electro-dialysis (EDBPM) for converting GLNa into GLH

The EDBPM cell made of polytetrafluoroethylene (PTFE), consists of 4 compartments (catholyte, anolyte, comp. 1, and comp. 2), separated by two pieces of CEM and BPM as shown in Figure 1. Parallel-cum-series flow arrangement was used separately for each compartment. Peristaltic pumps were used to feed the solution of electrolyte (500 cm<sup>3</sup>) in a recirculation mode into the respective compartments with a constant flow rate (0.006 m<sup>3</sup>/h) to maintain the turbulence. Precious metal oxide coated titanium sheet (TiO<sub>2</sub> sheet coated with a triple precious metal oxide (titanium-ruthenium-platinum); of 6.0  $\mu m$  thickness, and  $8.0 \times 10^{-3}$  m<sup>2</sup> effective area) obtained from Titanium Tantalum Products (TITAN, Chennai, India), were used as cathode and anode. A DC power supply (Aplab India, model L1285) was used to apply a constant current and resulting voltage was recorded with time using a digital multimeter. The whole setup was placed at ambient condition (30 °C) without any additional temperature control. The  $Na_2SO_4$  solution (0.10 M) was recirculated through electrode compartments, while distilled water was initially fed into comp.1 and the desired concentration of GLNa solution into comp. 2. The pH and conductivity of each stream output were regularly monitored, while the change in concentrations of NaOH was monitored by acid-base titration. GLH concentration in comp. 2 was determined by a UV-visible spectrophotometer at  $\lambda_{max}$ =660 nm wavelengths at definite time intervals.

### 2.4. Three compartments electro-membrane reactor (EMR-3) for *in situ* ion substitution of GLNa into GLH

EMR-3 was composed of three compartments, i.e. central compartment (CC), catholyte and anolyte, separated by two pieces of CEM as shown in Figure 2. All other accessories of the cell were similar to the EDBPM cell. Three storage tanks and pumps were used to continuously feed CC and electrode streams ( $5.0 \times 10^{-4}$  m<sup>3</sup> each) in recirculation mode with a 0.006 m<sup>3</sup>/h constant flow rate. Under polarized conditions,  $H^+$  ions were produced at anode by oxidative water splitting, migrated to CC through CEM and *in situ*  $Na^+$  substituted with the formation of GLH. Substituted  $Na^+$  in CC migrated towards the cathode and produced NaOH in the catholyte. The variation in pH

and conductivity of the all compartments were regularly monitored. Changes in NaOH concentration in the catholyte was determined by acid–base titration. The GLH concentration in CC was determined by a UV–visible spectrophotometer at  $\lambda_{\text{max}}=660$  nm wavelengths at a time interval of 30 min.

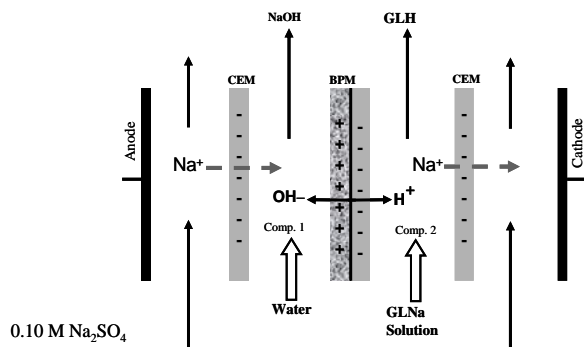


Fig. 1. Schematic diagram of EDBPM cell for the conversion of GLNa into GLH and NaOH.

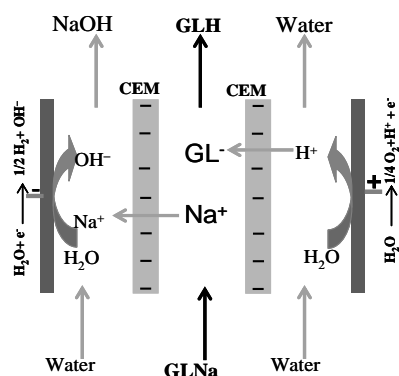


Fig. 2. Schematic presentation of electrochemical principles for possible in situ ion substitution/separation for producing GLH in EMR-3.

### 3. Results and discussions

#### 3.1. Membrane preparation and characterizations

CEMs and composite BPMs were prepared by the thin film casting and evaporation technique [32]. For the preparation of BPM, a heterogeneous anionic layer of desired thickness (100  $\mu\text{m}$ ) was casted onto a clean glass plate and dried. After coating the surface with interfacial layer, a cationic layer of SPEEK with the same thickness was also coated. The FTIR spectrum of CEM (SPEEK) was depicted in Scheme S4 in supporting information. The characteristic absorption band at 1590–1410  $\text{cm}^{-1}$  with a sharp to medium intensity was aroused due to the aromatic C–H stretching vibrations. Characteristic peaks of 1,2-disubstituted and 1,2,4-trisubstituted aromatic moiety were assigned at 2040–1914  $\text{cm}^{-1}$  [33]. The peak at 1710  $\text{cm}^{-1}$  was attributed to the carbonyl group, while stretching band at 1024  $\text{cm}^{-1}$  was observed due to the O=S=O vibrations of sulfonic acid group [34]. The band at 1283–1000  $\text{cm}^{-1}$  was observed due to in plane C–H deformation bands. The FTIR study confirmed sulfonation of PEEK.

The physicochemical and electrochemical properties of CEM and BPM are presented in Table 1. The membranes exhibited good water content, IEC and counter-ion transport numbers in the membrane phase with high conductivity under the operating conditions. Properties of CEM are in good agreement with the best-known ion-exchange membranes [35]. For developing an electro-membrane process; the knowledge of membrane conductivity under actual operating conditions is an essential parameter. The variation in  $k_m$  values for CEM and BPM in equilibration with NaCl and GLNa solutions of different concentrations is depicted in Scheme S5 (supporting informations). The  $k_m$  values for both membranes (CEM and BPM) were increased with equilibrating electrolyte concentration, and dependent on the ionic strength at the membrane/solution interface zone. The  $k_m$  values in equilibration with GLNa solution were low in comparison with NaCl solution due to low dissociation of GLNa. Low conductivity BPM in

comparison with CEM may be attributed to an increase in thickness due to the formation of a composite structure. Furthermore, physicochemical and electrochemical properties of CEM and BPM suggested their suitability for EDBPM and EMR-3 under GLNa and GLH environments.

Table 1  
Physico- and electro-chemical properties of CEM, AEM and BPM.

Properties	CEM	AEM	BPM
Thickness ( $\mu\text{m}$ ) <sup>a</sup>	150	150	200
Water content (%) <sup>b</sup>	32.9	24.2	27.3
Ion-exchange capacity (mequiv./g of dry membrane) <sup>c</sup>	0.96	1.27	---
Counter-ion transport number <sup>d</sup>	0.96	0.94	---
Permselectivity <sup>e</sup>	0.94	0.91	---
Conductivity <sup>f</sup> ( $\text{mS cm}^{-1}$ )	27.2	12.5	12.92

<sup>a</sup> Uncertainty for measurements: 1.0  $\mu\text{m}$ .

<sup>b</sup> Uncertainty for measurements: 0.1%.

<sup>c</sup> Uncertainty for measurements: 0.01 mequiv./g of dry membrane.

<sup>d</sup> Measured by membrane potential in equilibration in with 0.01 M and 0.1 M NaCl solutions.

<sup>e</sup> estimated from Counter-ion transport number.

<sup>f</sup> Uncertainty for measurements:  $0.01 \times 10^{-3} \text{ S cm}^{-1}$ .

#### 3.2. EDBPM for in situ ion substitution of GLNa

EDBPM experiments for in situ ion substitution of GLNa into GLH were carried out under the different applied current density (2.5–5.0  $\text{mA cm}^{-2}$ ). A schematic diagram of EDBPM is presented in Figure 1. GLNa solutions of different concentrations (0.15–0.17 M) were used as initial feed of comp. 2.  $\text{Na}_2\text{SO}_4$  solution (0.10 M) was recirculated into both electrode compartments, while deionized water into comp. 1. Variation of cell voltage with time at different current density during EDBPM is depicted in Scheme S6 (supporting information) as a representative case. At constant applied current density, cell voltage initially decreased and attended the limiting value. The voltage drop across the membrane depends on Donnan and diffusion potential at the solution-membrane interface and solution resistance. In the beginning, deionized water passing through comp. 1, offered high electrical resistance and high voltage drop was observed. Progressively, with ion formation ( $\text{OH}^-$  and  $\text{H}^+$ ) due to water splitting at the interfacial zone of BPM, ionic mobility in comp. 1 increased. As a result, electrical resistance offered by comp. 1 was continuously decreased with time. Due to water splitting at the interfacial zone of BPM, the formation of NaOH and GLH in comp. 1 and 2 were further assessed by the variations in pH and relevant data are presented in Figure 3. Initially, approximately pH of 7 was recorded for both streams but later it was increased in comp. 1 due to the formation of  $\text{OH}^-$  and thus NaOH. In comp. 2,  $\text{H}^+$  formed because of water splitting at the interfacial zone of BPM and substituted  $\text{Na}^+$ . These observations verified the process of EDBPM presented in Figure 1.

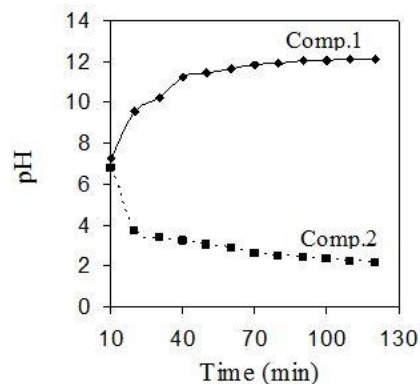


Fig. 3. Variations of pH in comp. 1 and 2 with time at 3.75  $\text{mA cm}^{-2}$  applied current densities, and GLNa solution (0.15M) as feed of comp. 2 in EDBPM.

The rate of water splitting or ion substitution ( $J$ ) during EDBPM/EMR-3

can be defined as the rate of NaOH concentration change and NaOH in comp. 1 or rate of GLH formation in comp. 2. Using Equation 3,  $J$  values were estimated from concentration changes of GLH or NaOH, considering negligible volume variations (water) transported across the membrane [26,27].

$$J = \frac{V_a}{A} \frac{C_t - C_0}{\Delta t} \quad (3)$$

where  $C_0$  and  $C_t$  are the initial and final concentration of NaOH or GLH (mol  $m^{-3}$ ),  $\Delta t$  is the time allowed (s),  $V_a$  the total volume ( $0.50 \times 10^{-3} m^3$ ), and  $A$  is the effective membrane area ( $8.0 \times 10^{-3} m^2$ ). Rate of water splitting or formation of NaOH ( $J$ ) during EDBPM is presented in Figure 4-A, as a function of electricity passed (Coulombs) at different current densities (2.5-0-5.0 mA  $cm^{-2}$ ). Initially,  $J$  values increased linearly with electricity passed afterwards limited due to unavailability of GLNa in comp. 2 or depletion in  $Na^+$  concentration for the formation of GLH and NaOH.

Recovery of the product (GLH) is an important parameter to examine the economic feasibility of any process and is defined as:

$$GLH \text{ recovery } (\%) = \frac{C_p V_p}{C_{0F} V_{0F}} \times 100 \quad (4)$$

where  $V_{0F}$  and  $V_p$  are the initial and final volume of comp. 2,  $C_{0F}$  is the initial concentration of GLNa in comp. 2 and  $C_p$  is the final concentration of GLH in comp. 2. GLH recovery at different GLNa feed concentration of comp. 2 was studied as a function of electricity passed (Coulombs) (Figure 4-B). GLH recovery decreased with an increase in GLNa feed concentration because of enhanced water splitting at the interfacial zone of BPM under a lower electrolytic environment (highly resistive). Furthermore, about 57-87% recovery of GLH was achieved in EDBPM under operating conditions.

Energy consumption ( $W$ ) and current efficiency (CE) are also important parameters to assess the economic feasibility of the electrochemical process (EDBPM/EMR-3) for their practical applications. The energy consumption ( $W$ , kWh  $kg^{-1}$  for producing GLH or base) in EDBPM/EMR-3 may be obtained by [27]:

$$W (kWh kg^{-1}) = \int_0^t \frac{V I dt}{m} \quad (5)$$

where  $V$  is the applied potential (volt),  $I$  the current,  $t$  the time allowed, and  $m$  is the weight of NaOH or GLH produced. CE may be defined as the fraction of Coulombs utilized for the water splitting and electro-migration of ions:

$$CE (\%) = \frac{m n F}{M Q} \times 100 \quad (6)$$

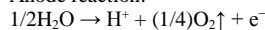
where  $F$  is Faraday constant,  $M$  the molecular weight,  $n$  is stoichiometric number ( $n = 1$  in this case), and  $Q$  is the electricity passed (Coulombs). Energy consumption, CE (%) and GLH recovery (%) values are presented in Table 2 to assess the water splitting, formation of GLH and base in EDBPM. CE and recovery of GLH were decreased with the applied current densities while energy consumption increased for 0.15 M GLNa solution as the feed of comp. 2. Under optimum operating conditions (after passing  $1.8 \times 10^3$  C electricity), CE and  $W$  were found to be 87.2% and 3.7 kWh  $kg^{-1}$ , respectively corresponding to 87% recovery of GLH. Relatively low CE may be explained in terms of gluconate ion ( $GL^-$ ) leakage through a BPM from comp. 2 to comp. 1 (Figure 5).  $GL^-$  leakage was very small (2-5%) at a 3.75 mA  $cm^{-2}$  constant current density, and increased with it or GLNa concentration in the feed. Such negligible  $GL^-$  leakage may not affect the product purity and deteriorate the process performance of EDBPM. Also, relatively low CE and GLH recovery and high energy consumption for converting GLNa into GLH in EDBPM reduced the feasibility of the process. Thus, there was urgency to develop an alternate process for in situ ion substitution of GLNa for producing GLH by an eco-friendly manner.

### 3.3. In Situ ion substitution of GLNa in EMR-3

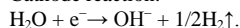
The electrochemical principle of EMR-3 used for in situ ion substitution of GLNa is described in Figure 2. This process involved three stages: (i) generation of  $H^+$  and  $OH^-$  ions by oxidative and reductive water splitting at the anode and cathode, respectively; (ii) electro-migration of  $H^+$  through CEM from anolyte to the central compartment (CC) and in situ substitution of  $Na^+$  by  $H^+$  and formation of GLH; (iii) electro-migration of  $Na^+$  from CC to catholyte through CEM and subsequent formation of NaOH. In this process, in situ ion substitute. Relatively low CE with high  $W$  was observed at high

current density. Data presented in Table 3 revealed reduction in CE and an increase in  $W$  with GLNa feed concentration of CC at constant applied current density was achieved by coupled principles of electrode polarization and electrodialysis and may be defined as electro-electrodialysis. In this case, GLNa/GLH was separated from electrodes by CEM, thus electro-migration of the gluconate ion ( $GL^-$ ) towards cathode was negligible because of the strongly charged nature of CEM. Furthermore, about 1-2% (v/v) concentration of  $GL^-$  in the anolyte was measured by using a UV-visible spectrophotometer. In addition, electrode reactions for EMR-3 may be written as:

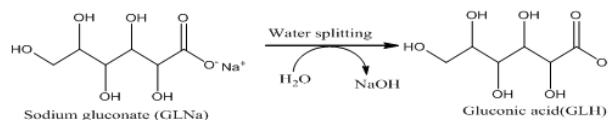
Anode reaction:



Cathode reaction:



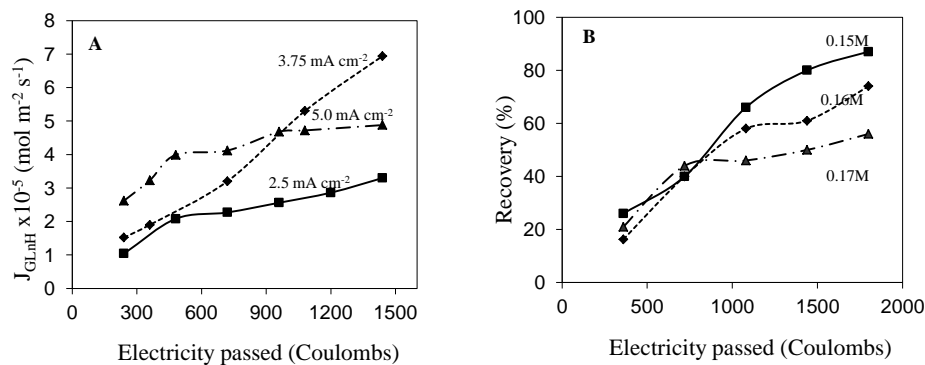
Electrochemical reactions occurring at both electrodes were a water splitting process. One electron produced at the anode was consumed at the cathode, and this may be treated as a one-electron process. Overall electrochemical reaction for in situ ion substitution GLNa can be written as:



*In situ* ion substitution in GLNa solutions (0.15-0.17 M as initial feed of CC) were carried out in the EMR-3 cell at different current densities (2.5-5.0 mA  $cm^{-2}$ ). Distilled water was passed through the anolyte and catholyte in a recirculation mode of operation. The variations in cell voltage with time under different experimental conditions are presented in Scheme S7 (supporting information), as a representative case. At constant current density, cell voltage was initially high because of electrical resistance offered by distilled water in electrode compartments. Initial resistance offered by electrode compartments was dominating, while resistance of CC was low due to GLNa solution. Progressively, cell voltage decreased because of electrode polarization and the formation of  $H^+/OH^-$ . Afterwards, resistance offered by the catholyte and anolyte was reduced, while resistance offered by CC was dominated due to the formation of a weak acid (GLH). During the electrochemical process, variations in pH of catholyte, anolyte, and CC at constant current density (3.75 mA  $cm^{-2}$ ) for 0.15M GLNa solution as feed of CC is depicted in Figure 6, as a representative. The pH of the anolyte and CC were reduced due to the formation of  $H^+$  and GLH, respectively, while pH of the catholyte was increased due to the formation of NaOH. These observations also verified the electrode polarization and electro-transport phenomena presented in Figure 2.

The rate of in situ ion substitution of GLNa ( $J$ ) in EMR-3 may be assessed by the rate of migration of  $H^+$  from anolyte to CC and simultaneous exchange of  $Na^+$  or formation rate of NaOH in the catholyte.  $J$  values were estimated from a concentration change of GLH in the CC or concentration changes of NaOH in the catholyte, using Equation 3.  $C_{0p}$  and  $C_f$  are the initial and final concentration of GLH in CC (mol  $m^{-3}$ ). Relevant data for  $J$  are presented in Figure 7-A. Initially,  $J$  values increased with electricity passed due to a negligible back diffusion of  $Na^+$  from the catholyte to CC because of a low concentration of  $Na^+$  in the CC. The rate of ion substitution was also increased with current density and GLNa feed concentration. During the whole process, electro-neutrality conditions were maintained. After attaining maxima,  $J$  values further reduced because of enhanced back diffusion of  $Na^+$  from the catholyte to CC. Furthermore, the rate of in situ ion substitution was highly dependent on applied current density and initial feed GLNa concentration in CC. Recovery of GLH reduced with GLNa feed concentration in CC. More than 90% recovery of GLH (Figure 7-B) by EMR-3 was higher in comparison with EDBPM (Figure 4-B) under similar conditions. The high recovery and rate of ion substitution in EMR-3 indicated suitability of the process for industrial exploitation. To evaluate the economic feasibility for in situ ion substitution of GLNa in EMR-3,  $W$  and CE (%) data under different experimental conditions are presented in Table 3. Energy consumption increased while CE decreased with the applied current densities under similar conditions. At high applied current density, enhanced formation of  $H^+/OH^-$  results in fast migration of  $H^+$  from the anolyte to CC and thus high



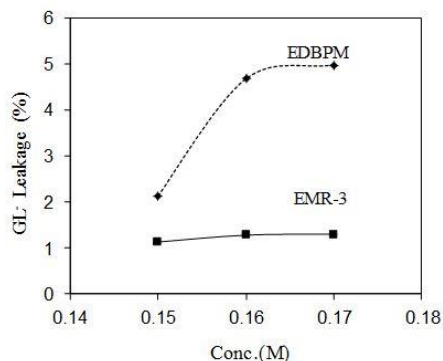


**Fig. 4.** In EDBPM: (A) Variation of  $J_{GLH}$  with time at different applied current density with 0.15M GLNa solution as initial feed of comp. 2; (B) variation of recovery of GLH at 3.75  $mA cm^{-2}$  applied current density and varied concentration of GLNa solution as initial feed of comp. 2.

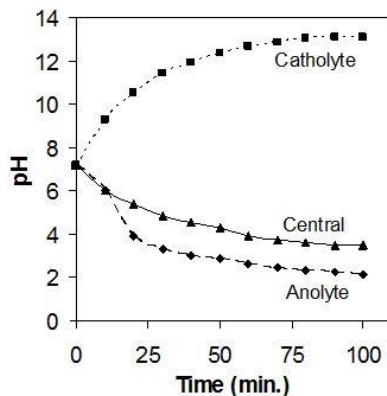
**Table 2**

GLH recovery, Current efficiency, and energy consumption, data for conversion of GLNa into GLH and NaOH in EDBPM.

Applied current density ( $mA cm^{-2}$ )	Feed GLNa in Comp.2(M)	GLH Recovery (%)	Current Efficiency (%)	Energy consumption ( $kWh kg^{-1}$ )
2.50	0.15	87	90.6	3.01
3.75	0.15	85	86.8	3.62
5.00	0.15	66	82.3	6.30
3.75	0.15	87	87.2	3.70
3.75	0.16	74	79.1	4.30
3.75	0.17	56	63.7	4.71



**Fig. 5.** Gluconate ion (GL) leakage vs GLNa concentration in feed in EMR-3 and EDBPM process at 3.75  $mA cm^{-2}$  applied current density.



**Fig. 6.** Variations of pH for catholyte, anolyte and CC output with time at 3.75  $mA cm^{-2}$  applied current density and GLNa solution (0.15 M) as feed of CC in EMR-3.

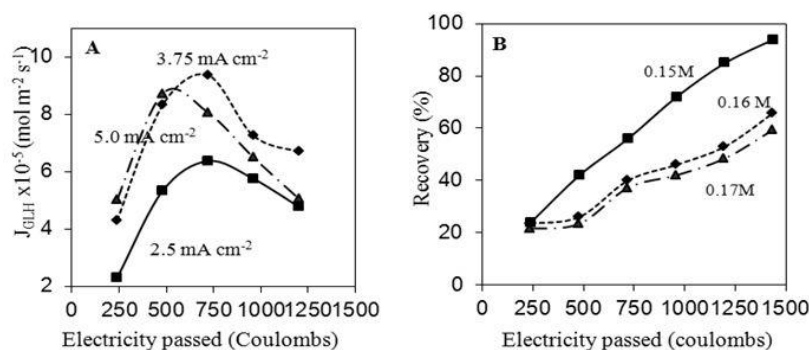


Fig. 7. In EMR-3: (A) Variation of  $J_{GLH}$  with time at different applied current density with 0.15M GLNa solution as initial feed of comp. 2; (B) variation of recovery at 3.75 mA cm<sup>-2</sup> applied current density and varied concentration of GLNa solution as initial feed of comp. 2.

Table 3

Current efficiency, energy consumption and GLH recovery data for *in situ* ion substitution/ separation of GLNa in EMR-3.

Applied current density (mA cm <sup>-2</sup> )	Feed GLNa in CC	GLH Recovery (%)	Current Efficiency (%)	Energy consumption (kWh kg <sup>-1</sup> )
2.50	0.15	96.4	93.4	1.07
3.75	0.15	92.3	92.7	1.31
5.00	0.15	71.1	89.3	2.14
3.75	0.15	94.2	93.7	1.28
3.75	0.16	66.1	88.5	1.60
3.75	0.17	59.2	84.3	1.81

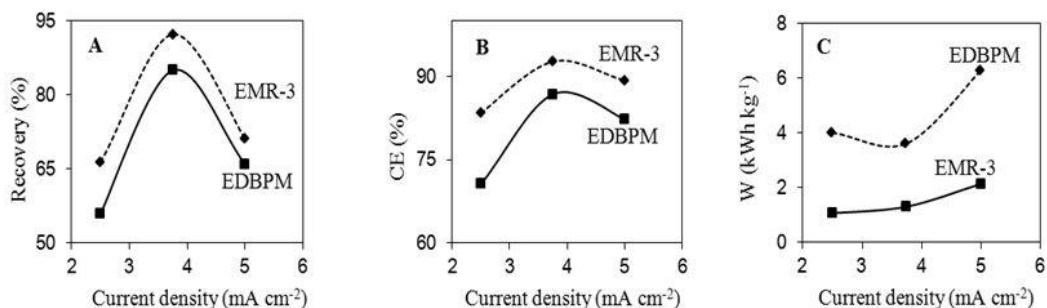


Fig. 8. Comparison of CE, GLH recovery and energy consumption (W) in EDBPM and EMR-3, with 0.15M GLNa solution as initial feed and under similar other operating conditions.

GLH formation rate was observed. Relatively low CE with high W was observed at high current density. Data presented in Table 3 revealed reduction in CE and an increase in W with GLNa feed concentration of CC at constant applied current density. Reduction in CE may be explained due to relatively low electro-transport of Na<sup>+</sup> in comparison with H<sup>+</sup> because of the fast mobility of the latter one [36]. Earlier reports revealed the relationship between proton migration and water flux in acidic conditions. It was observed that as the proton flux increased, water flux from the anodic side reduced. There was good agreement with the reported results and our findings [37]. Thus, concentration of GLNa, nature of CEM and its permselectivity are also important parameters. These results suggested that EMR-3 is an efficient and simple process for *in situ* substitution of GLNa. Further, to assess the suitability of EMR-3, its process efficiency parameters will be compared with the BPMED.

#### 3.4. Comparison between EDBPM and EMR-3 for process efficiency and recovery of GLH

The currently traditional process used for the production of gluconic acid is based on fermentation of glucose. Glucose was converted into glucono- $\delta$ -lactone followed by base hydrolysis in the presence of *Aspergillus niger* bacteria that transformed into sodium gluconate. Further, GLH was obtained by acidification with sulfuric acid and separation of GLH and Na<sub>2</sub>SO<sub>4</sub>. In this work, ion substitution of GLNa was achieved by EDBPM and EMR-3 for producing GLH and process efficiencies (W, CE and recovery of GLH) of

both were compared in Figure 8-A to C under similar experimental conditions. CE and GLH recovery was high while energy consumption was low for EMR-3 in comparison with EDBPM. Thus, EMR-3 is a more efficient process than EDBPM for *in situ* ion substitution of GLNa for producing GLH. Close to 94% CE and GLH recovery values for EMR-3 indicated its suitability and efficient nature. Furthermore, the production of NaOH in catholyte was a spin off. Despite the suitability of EMR-3 for industrial exploitation, one has to completely optimize the process for maximum CE with low energy consumption, and high recovery of GLH along with suitable CEM, all of which has high impact on the economic feasibility of this process.

#### 3. Conclusions

Herein, we reported CEM and BPM with good physicochemical and electrochemical properties suitable for developing EDBPM and EMR-3 for *in situ* ion substitution of GLNa for producing GLH based on the principles of electro-electrodialysis. Membrane conductivity values of CEM and BPM in equilibration with either NaCl or GLNa solution, suggested their suitability for use under these environments in EMR-3 or EDBPM. Results showed that EMR-3 proved a promising tool for *in situ* ion substitution of GLNa with high CE (93%) and low energy consumption (1.28 kWh/kg of GLH produced). The EMR-3 process performances were dependent feed GLNa concentration in CC, applied current density and electrochemical properties of CEM/BPM. Ion substitution of GLNa was also achieved by EDBPM and its process

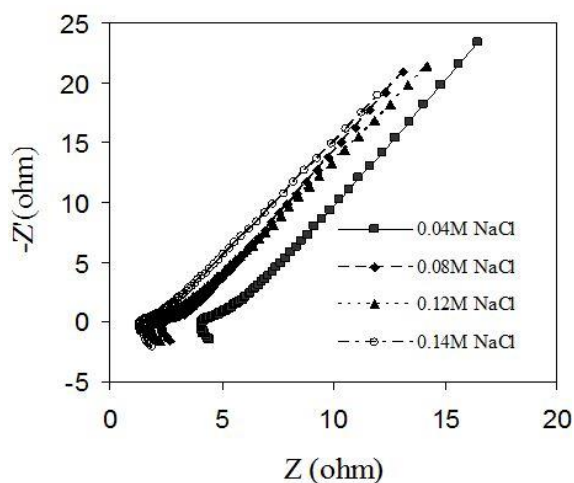
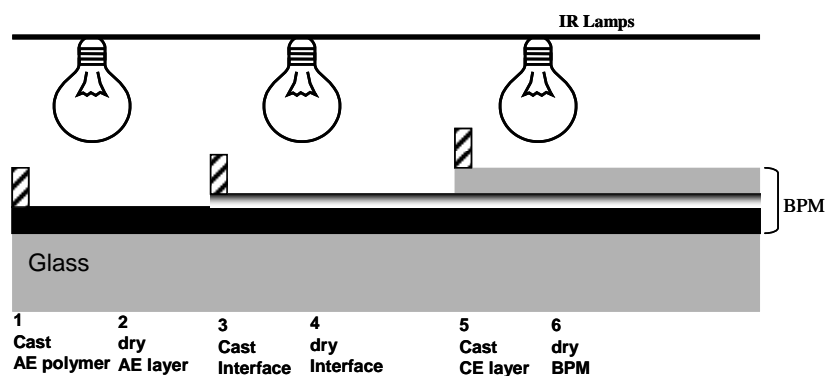
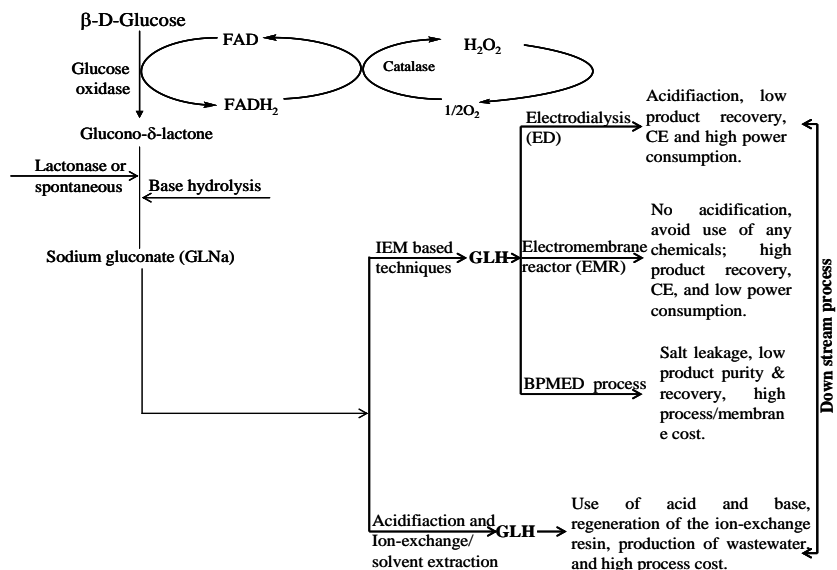
efficiency was compared with EMR-3 under similar experimental conditions. It was concluded that EMR-3 is a more efficient process in comparison with EDBPM for in situ ion substitution of GLNa producing GLH. The production of NaOH as a byproduct in the cathode stream is a spinoff of the EMR-3 and EDBPM.

Furthermore, process performances were investigated in the laboratory scale for the conversion of GLNa into GLH in EDBPM or EMR-3 to avoid acidification and further separation of GLH and Na<sub>2</sub>SO<sub>4</sub>. Novel reported EMR-3 is completely green in nature without the generation of waste mass. In this process, ion substitution occurred through water splitting without the use of chemicals, which provide an eco-friendly and economic viable route for the down-stream process involved in the production of GLH.

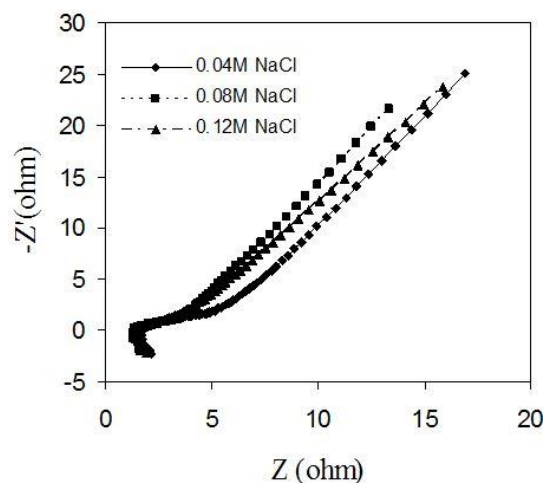
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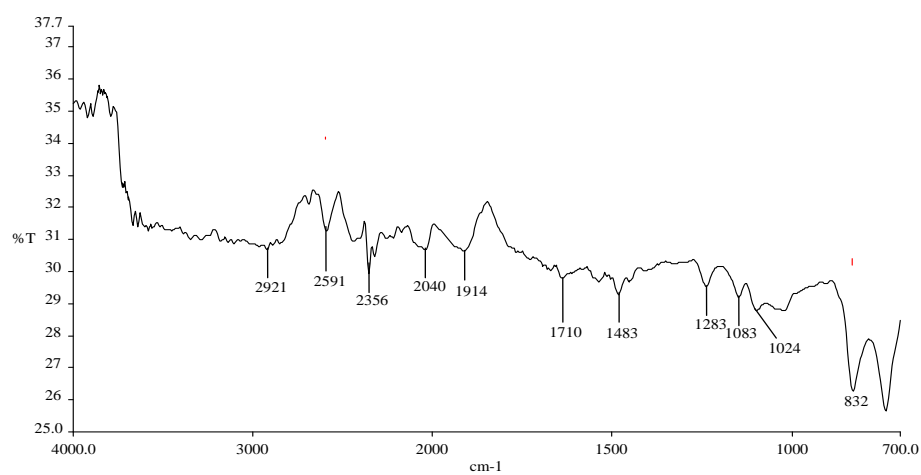
## Supporting Information



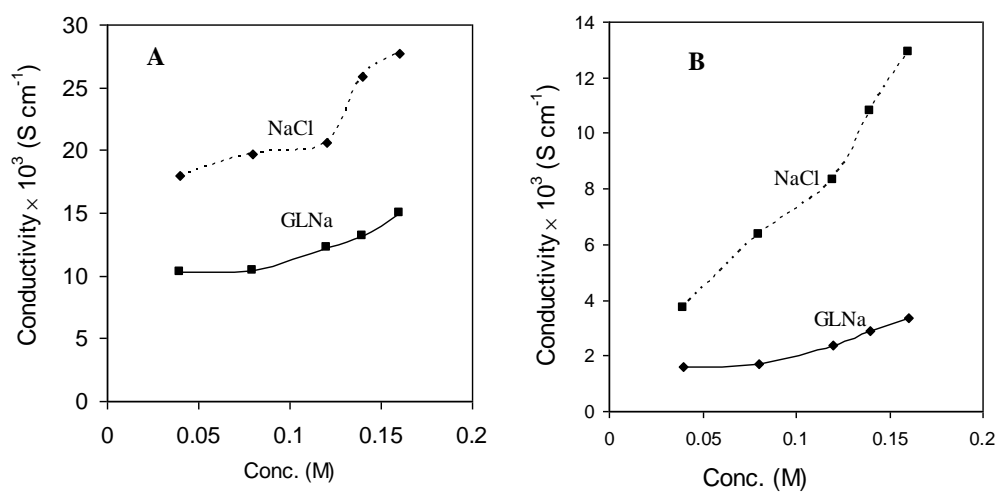


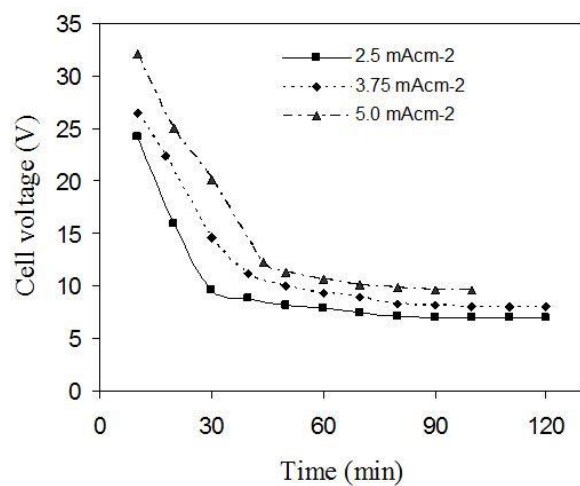


Scheme S4. Nyquist plots for CEM in NaCl solution of different concentration.

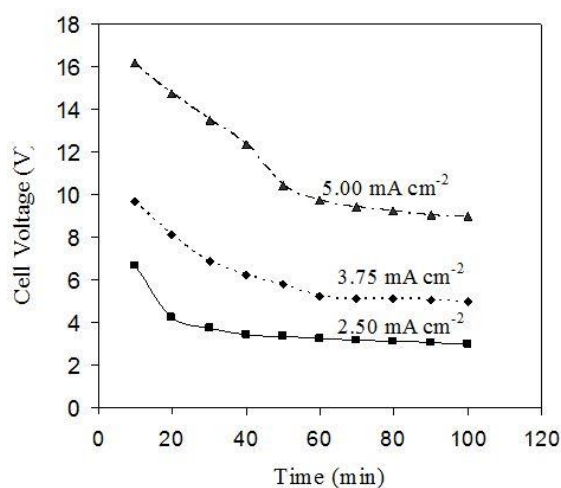


Scheme S5. FTIR spectrum of CEM (SPEEK).

Scheme S6. Membrane conductivity ( $\text{km}$ ) values for: (A) CEM; and (B) BPM, in equilibration with NaCl and GLNa solutions of varied concentrations.



**Scheme S7.** Variation in cell voltages with time during the conversion of sodium gluconate (GLNa) into gluconic acid (GLH) in EDBPM process and feed in comp. 2 was 0.15 M GLNa solution at different applied current densities.



**Scheme S8.** Variation in cell voltages with time during the conversion of GLNa into GLH in EMR-3, with 0.15 M GLNa solution as feed of CC at different applied current densities.