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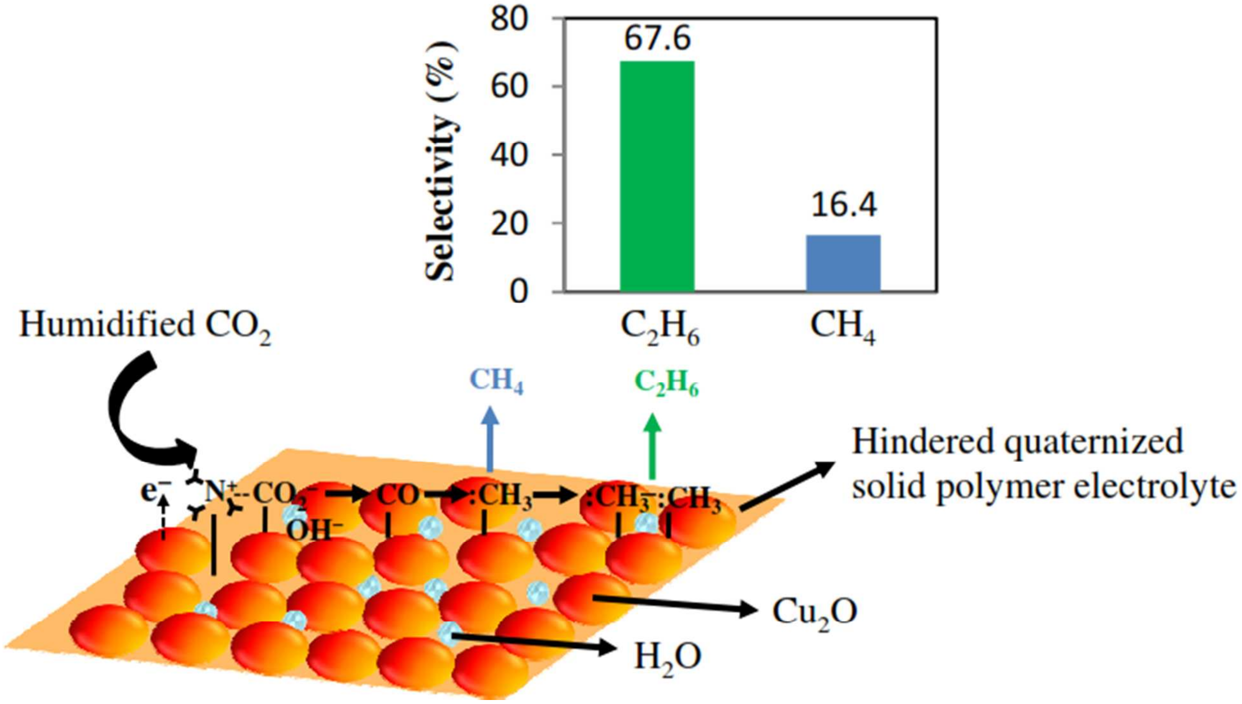

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PAPER

Electrochemical conversion of CO_2 to fuels: Tuning of reaction zone using suitable functional group in solid polymer electrolyte

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The electrochemical reduction of gaseous CO_2 is studied for the first time using sterically hindered bulky quaternary ammonium ion in solid polymer matrix at room temperature and atmospheric pressure in a developed electrochemical reactor. Some new insights are developed for the effective reaction process. It is found that the reaction zone can be tuned in a great extent with the help of fixed functional groups attached in the solid polymer. To illustrate the concept, solid polymer electrolytes with the same backbone and different fixed functional groups are synthesized. It is found that only change in functional group in the membrane can dramatically change the efficiency and selectivity of the reaction products. Moreover, the suitable groups may increase the mass transfer of CO_2 at the reaction interface and may help as a co-catalyst. This work may open a new approach for the development of next generation process for gaseous CO_2 electroreduction to fuels, which is a present need.

Introduction

The excessive anthropogenic emissions of CO_2 resulting from the combustion of fossil fuels are causing the climate change.[1] Current Intergovernmental Panel on Climate Change (IPCC) projections reports that atmospheric CO_2 concentrations will increase over this century, reaching 730–1020 ppm by the year 2100. Major technological approaches to deplete CO_2 from the atmosphere follow either capture and sequestrate CO_2 or convert CO_2 to fuel.[2-4] In recent years, CO_2 conversion using electrochemical reduction of CO_2 (ERC) has attracted great attention for its several advantages: (i) the process can be carried out at room temperature and pressure[5]; (ii) overall chemical consumption can be minimized to simply water or wastewater for the proton source[6]; (iii) renewable energy may be used to drive the process, which can ultimately be stored as reaction products[7]; (iv) the compact electrochemical system can easily be scaled-up; and (v) the by-product (H_2) of ERC may be minimized.

Over the last several decades, the research is being focused especially on electrode materials using absorbed CO_2 in aqueous and non-aqueous electrolytes and various reviews are published.[8-17] It is studied and reported that the electrocatalystsplay a critical role on the product distribution and Faradaic efficiency in the ERC. It has been reported that formation of CO_2 anion radical ($CO_2^{\bullet-}$) is the rate determining step for the reduction of CO_2. The electrical potential for $CO_2/CO_2^{\bullet-}$ is -1.9V vs. SHE through single electron pathway. However, the requirement of this much high energy may be reduced by proton or hydroxyl ion assisted multi-electron reduction of CO_2.[18] However, it is well known that hydrogen evolution reaction (HER) is competitive to CO_2 electroreduction in the presence of aqueous electrolyte solution. The electrochemical reduction of CO_2 in aqueous solutions has been reported by many authors.[19-21] A few authors studied the role of liquid electrolyte for ERC and found that the ions (cations or anions) in the electrolyte and supporting salts influence the ERC greatly.[22-25]

Saeki et al.,[24] studied the effect of supporting electrolytes on the ERC in CO_2+methanol system. CO with a Faradaic efficiency of 86% was the major CO_2 reduction product when tetrabutylammonium (TBA) salts were used as supporting electrolyte in ERC. Methylformate was the major CO_2 reduction product when lithium salts were used as the supporting electrolyte with a significant amount of H_2 generation. Grace et al.,[26] investigated ERC in TBA perchlorate in methanol electrolyte, where HCOOH and CH_3COOH were found primarily with Faradaic efficiencies of 30.4% and 63.0%, respectively. Liquid electrolytes were used, which offered large ohmic resistance, leakage from the reactor, liquid product dilution or complex separation of the products, as well as significant hydrogen evolution. Therefore, researchers are investigating solid polymer electrolytes to overcome these challenges of the liquid electrolyte.[27-32] Not only the above challenges may be overcome but the solid polymer electrolye (SPE) may be tuned as per the requirement. It has been found that the SPE affect the ERC process. In our earlier study, it was found that cationic and anionic SPEs have some effect on the efficiency of the ERC.[28]However, neither know-how of the process is clear nor the potential effect on the selectivity is known. Therefore, this paper is aimed to find out whether the functional groups on the SPE affect the ERC and the possible reason. Novelty of this paper is to use the knowledge of amines (in SPE) for the CO_2 absorption, which might be useful to capture the CO_2 at the functional group, and simultaneously convert the CO_2 to the product with high efficiency due to enhanced mass transfer pertaining at the reactive

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site. Thus here we report for the first time, the solid polymer electrolyte having suitable functional groups, which can affect the product selectivity to accomplish efficient ERC using gaseous CO_2.

To verify the proposed novel approach, branched polyethylenimine (PEI) having amine groups was chosen forsynthesizing quaternized PEI (QPEI) in order to prepare anionic SPE. However, PEI does not have the film forming ability. Thus poly(vinyl alcohol) (PVA) was used as a polymer matrix so as to form SPE membrane. Two different SPEs were developed and evaluated for ERC. One SPE was developed with direct blending of PEI with PVA and doped with KOH (PEI/PVA/KOH), whereas the other one was developed with blending of quaternized PEI with PVA and doped with KOH (QPEI/PVA/KOH). Gaseous CO_2 instead of solubilized CO_2 was used in the electrochemical study. The product distribution, Faradaic efficiency, and selectivity of the products were evaluated to understand the rationale behind the process to generate reaction products along with the reaction mechanism.

Experimental

Materials

Polyethyleneimine (7,50,000 g.mol^{-1}) and polyvinyl alcohol (1,15,000 g.mol^{-1}) were procured from Sigma Aldrich, India. Pt/C (40wt.%) was procured from Electro-Chem., USA. Porous carbon paper (TGP-H-120) from Torayca was used as a support for electrode preparation. Other chemicals like bromopropane, glutaraldehyde, dimethylsulfoxide (DMSO) and potassium hydroxide (KOH) were procured from Merck, India. All the chemicals were used without further purification unless otherwise specified and de-ionized water was used in all the experiments.

Method

Synthesis of PEI/PVA/KOH and QPEI/PVA/KOH

Solutions (5wt.% each) of branched PEI and PVA were prepared in suitable solvents. The obtained solutions were mixed in 1:2 ratio of PEI and PVA. Then 10wt.% of glutaraldehyde (GA) solution was added as crosslinking agent for PVA. The membranes (thickness around 100µm) were prepared by solution casting technique. The prepared membranes were doped with KOH solution for atleast 24h and washed several times with de-ionized water to obtained alkaline SPE (PEI/PVA/KOH) as shown in Figure 1A. In a similar way, QPEI/PVA/KOH was synthesized. However, the PEI was first quaternized by adding bromopropane solution into PEI solution under stirring at 60 °C until clear homogeneous solution of quaternized PEI was obtained. Thereafter, the QPEI/PVA/KOH was synthesized in a similar way as PEI/PVA/KOH.

Characterization

The SPEs were characterized using different techniques to ascertain the quaternization as well as their suitability for the ERC process. FTIR spectra were recorded in 4 cm^{-1} of spectral resolution in the range of 510–4000 cm^{-1} using a Perkin Elmer, Spectrum One, Fourier Transform Infrared Spectrometer. Through plane ionic conductivity was measured by AC impedance technique over a frequency range of 10 kHz to 100 mHz using a potentiostat (CHI6002B, CH Instruments, USA) in an ionic conductivity test apparatus as described elsewhere.[33] Ion exchange capacity, water uptake, and swelling of the SPEs were evaluated as per the standard test procedures given elsewhere.[34]

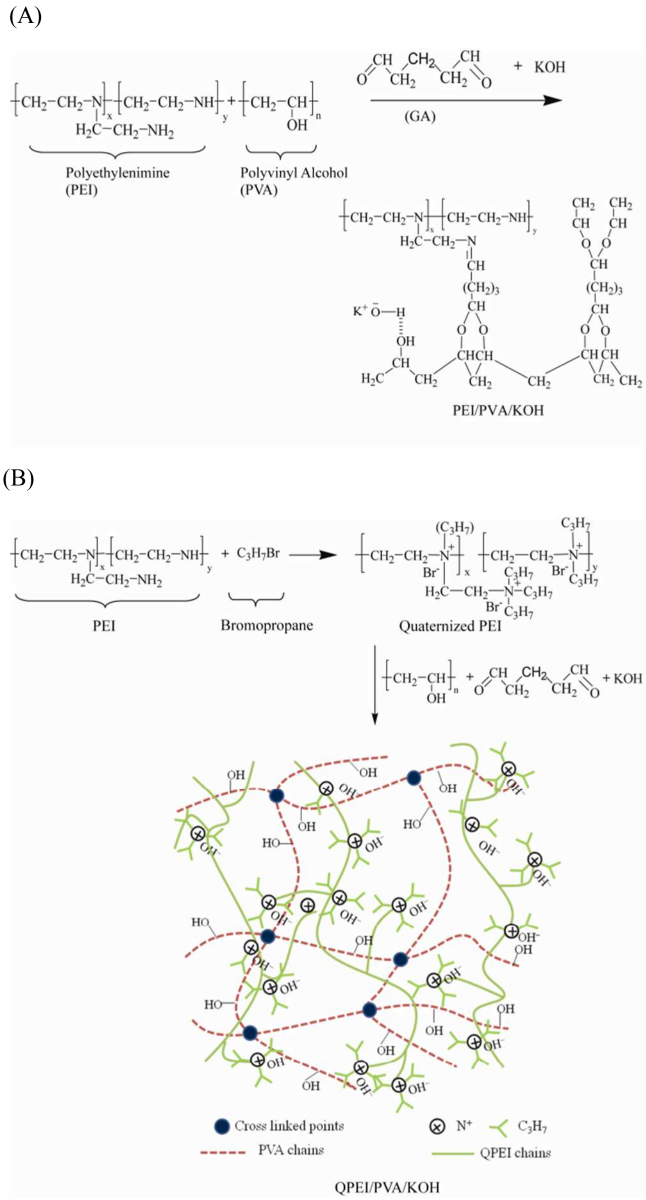

Figure 1. Structural representation of (A) PEI/PVA/KOHand (B) QPEI/PVA/KOH SPEs

The tensile strength of the membrane samples was evaluated as per ASTM D-882 at ambient condition using universal testing machine.

Experimental Setup

Figure S1 shows an experimental setup for ERC in which CO_2 gas (99.995%) was fed at the cathode (Cu_2O electrodeposited on carbon paper) side of the electrochemical reactor through a humidifier with a flow rate of 20 ml.min^{-1}.[28] Deionized water was fed as a reactant at the anode (Pt/C) side of the electrochemical reactor using peristaltic pump with a flow rate of 1.5 ml·min^{-1}. The cathode and anode outlets were connected to gas/liquid

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separators to separate the gas and liquid reaction products. The ERC was conducted at different electrical voltages for 25 minutes in pulse mode (chronoamperometry - pulse width 5 s). During the off-cycle of the voltage pulse, the current reduced to zero and thus because of no reaction, the formed products diffuse out easily.[28] The reaction productscollected from cathode outlet were analyzed by gas chromatograph (GC).All the experiments were performed at room temperature (25°C) and atmospheric pressure. Each experiment was performed with fresh electrodes as well as with a fresh SPE to rule out any side effect such as influence of ageing or poisoning of the electrode and SPE.

Analysis of Products

Products formed during ERC were analyzed using custom made GC (Figure S2). The H_2 and CO_2 gases were detected using thermal conductivity detector (TCD), CO (after passing through methanizer), and hydrocarbons (CH_4, C_2H_4, and C_2H_6) were detected using flame ionization detector (FID). The liquid product like methanol was analyzed by GC using packed column (Porapak-Q) in FID. The products from the ERC reactor were collected during 0-5, 5-10, 10-15, 15-20, and 20-25 minutes. The collected products for the stated time span were quantified by GC with the help of standard calibration curves (Figure S3). Total amount of the products collected during 25 min. is also shown while discussing the relevant figure. The Faradaic efficiency was calculated by determining the charge passed to produce a particular product with respect to the total charge passed during the experiment (sampling time).

Results and Discussion

SPEs Characterization

FTIR spectra of PEI/PVA and QPEI/PVA are shown in Figure 2. In both the cases due to the crosslinking of glutaraldehyde, a peak at 2836 cm^{-1} corresponding to C–H stretching related to aldehydes and another strong peak from carbonyl group (C=O) is observed at 1716 cm^{-1}. In the case of PEI/PVA SPE,a peak shown at 1635 cm^{-1} represents the formation of imine (C=N) linkage, which confirm that crosslinking was taken place between NH_2 sites of PEI polymer and crosslinked polyvinyl alcohol.[35] The quaternization of the PEI is confirmed by the disappearance of imine linkage at 1635 cm^{-1} and an increased intensity of the C–H stretching and deformation vibration bands at 1656 and 1461 cm^{-1} and the quaternary ammonium absorption band can be seen at 916 cm^{-1}.[36]

Figure 3 shows the different properties of PEI/PVA/KOH and QPEI/PVA/KOH. The ionic conductivity and ion exchange capacity of the SPEs are important properties. The ionic conductivity indicates the ease of the hydroxyl ion to transport from cathode to anode through the SPE, whereas ion exchange capacity signifies the replaceable ions (meq./gm of polymer) in the SPE. The branched QPEI was interpenetrated in the crosslinked PVA chains to form the semi-interpenetrating polymer network (s-IPN) structure as shown in the Figure 1. Therefore, the quaternization has a dominant influence on the ionic conductivity and tensile strength of the membranes (Figure 3). The ionic conductivity of QPEI/PVA/KOH was 10 times than the PEI/PVA/KOH. It may be because quaternary ammonium cation can have higher amount of loosely held hydroxide ions, which led to the higher ionic conductivity through Grotthuss mechanism in the electric field. It can be seen in the Figure 3A that the IEC of the SPE is affected by the quaternization and it increased significantly after quaternization. It may be due to the bulky quaternary ammonium ion has higher anion activation stability due to the longer distance between cation and anion and thus hydroxyl ions are loosely held with the quaternary ammonium ion and enhances the ion exchange capacity.[37] The electrostatic attraction between cation and anion will be weaker, resulting in more nucleophilic nature of the anion. In the case of PEI/PVA/KOH, solvation effects of primary and secondary amines increase the electron density on the amine nitrogen to a greater extent leads to higher water uptake and swelling. The hydrophilicity of the QPEI/PVA/KOH was reduced by introducing alkyl groups via quaternization, resulting in a slight decrease in water content as shown in Figure 3B. Therefore, the above results show that the membranes chosen for the ERC are suitable to be used as SPEs and thus evaluated in the electrochemical reactor and discussed in the further sections.

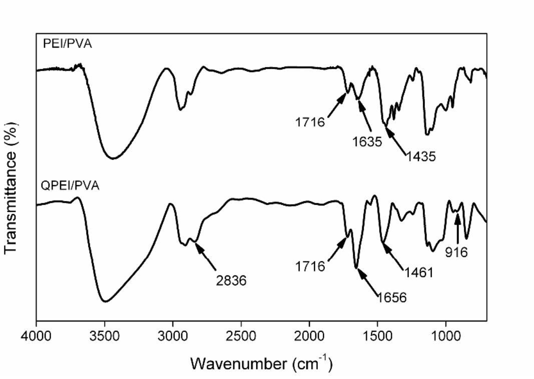

Figure 2. FTIR spectra of PEI/PVA and QPEI/PVA polymer

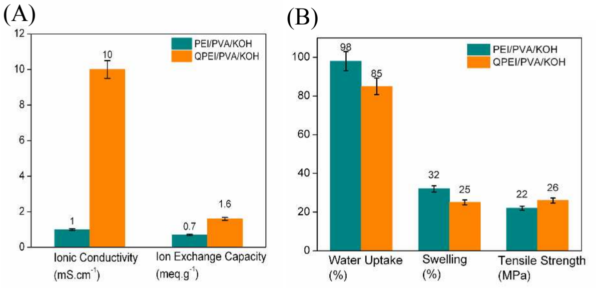

Figure 3. (A) Ionic conductivity and ion exchange capacity, and (B) water uptake, swelling and tensile strength of PEI/PVA/KOH and QPEI/PVA/KOH SPEs

Influence of Functional Groups in SPE on dERC

The gaseous CO_2 was fed into the electrochemical reactor and various products were obtained at different applied voltages in the range of 1.8 V to 3 V. Figure 4 shows the current density and the amount of the products formed as a function of applied voltage in the direct electrochemical reduction of CO_2 (dERC). It can be seen that the increase in voltage directly influences the current density and amount of product formed. However, the current density and amount of CH_4 formed increases upto a certain voltage depending upon the SPE used and on further

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voltage increase, CH_4 formation decreases and corresponding current density. In case of PEI/PVA/KOH (Figure 4A), CH_4 was the main product, whereas C_2H_6 and CH_4 were the major products for the QPEI/PVA/KOH (Figure 4B) along with comparatively minor quantities of CO, and CH_3OH in both the cases. Hydrogen gas was formed due to water electrolysis (a competitive reaction at the cathode) in both the cases as a by-product. However, the generation of H_2 gas was reduced as high as upto 50% when quaternized SPE was used for the dERC.

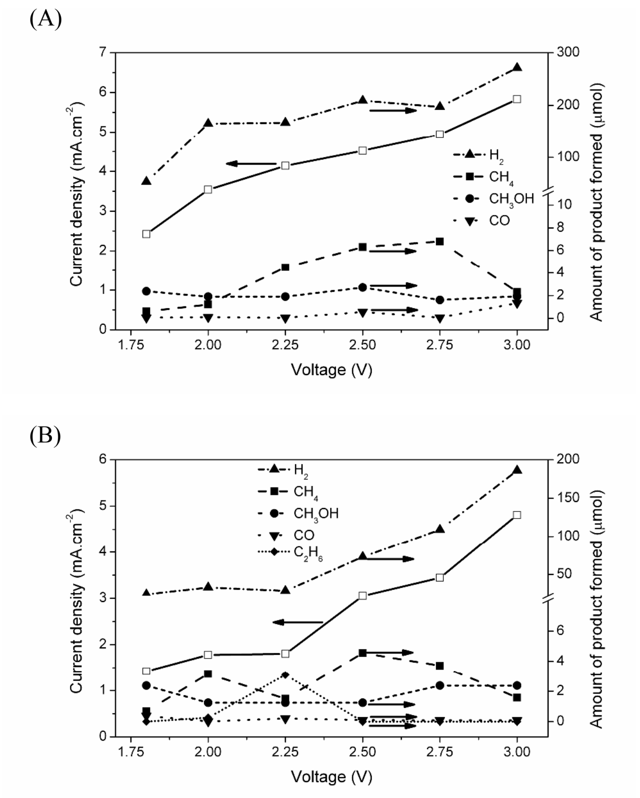

Figure 4. Current density and product distribution obtained as a function of applied voltage in the ERC using (A) PEI/PVA/KOH and (B) QPEI/PVA/KOH SPEs during 25min of electrolysis

Figure 4 shows that the current density increases with the increase in the applied voltage for both the SPEs, which indicate that the rate of the reactions increase with the increase in the applied voltage. The increased reaction rate corresponds to the increased electrical charge consumed by the various electrochemical reactions at the electrodes. In case of PEI/PVA/KOH SPE, current density increases from 2.42 mA.cm^{-2} at 1.8 V to 5.83 mA.cm^{-2} at 3 V, whereas 1.42 mA.cm^{-2} at 1.8 V to 4.81 mA.cm^{-2} at 3V are obtained using QPEI/PVA/KOH. Higher current density was observed for PEI/PVA/KOH as compared to QPEI/PVA/KOH at any of the voltages. However, it is interesting to note that though the experimental conditions were same except the functional group but the product formation was greatly influenced.

Based on the results, the process being conceptualized along with the reaction mechanism and is depicted in Figure 5. Figure 5A shows a representative cartoon of membrane electrode assembly having anode-SPE-cathode structures. In order to have good contact among these components, the assembly was

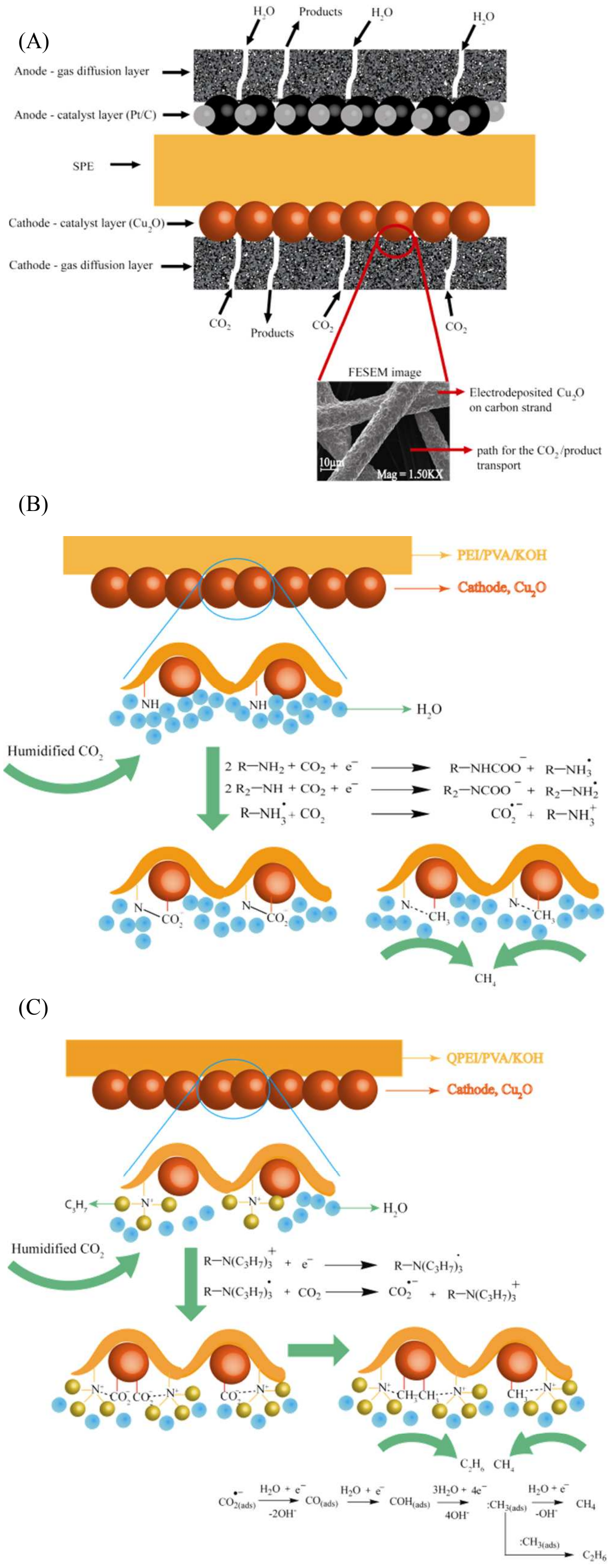

Figure 5. (A) Representation of membrane electrode assembly, (B) conceptualization of ERC using (B) PEI/PVA/KOH and (C) QPEI/PVA/KOH

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fabricated using hot press method. It can be seen that due to the hot press process, the SPE bulges in between the catalyst particles and can be seen in Figure 5A. The FESEM micrograph of the electroplated cathode on the carbon paper (Cu_2O/C) is shown inthe Figure 5A.The discontinuous nature (porous surface) of the electrodes was prepared to transport the reactants and products. The bulging of the polymer around the electrocatalyst is infact an added advantage as it provides high and effective three-phase boundary for electrochemical reactions. Figure 5B shows the PEI/PVA/KOH as SPE (having primary, secondary, and tertiary amines as shown in the Figure 1A). CO_2 reaching to the interface is absorbed by the amine group and its linear stable structure bends by forming the carbamate via intermediates possibly composed of the loosely-bound encounter complex and zwitterion.[38, 39] Moreover, the electrocatalyst present at the interface along with the solvated water molecules form the reaction product and hydroxyl ion. These hydroxyl ions move from cathode to the anode and transform to water and O_2 gas in the presence of the anode electrocatalyst. The quaternized SPE (QPEI/PVA/KOH) (Figure 5C) having bulky alkyl groups hinders the water molecules to get associated with the quaternary group and thus decreases the solvation effect due to weaker electrostatic interactions.[40] In case of QPEI/PVA/KOH SPE having bulky alkyl groups (Figure 1B), the incoming CO_2 does not form carbamate but ammonium group increases the CO_2 absorption capacity by forming an ion pair and/or bicarbonate.[24] The observations (Figure 4) to get low H_2production (by-product of ERC) for the quaternized SPE as well as formation of C_2H_6 by C-C coupling was might be due to low water availability at the interface. It is interesting to observe that the maximum amount of formation of CH_4 (peak value) shifted to the lower potential (2.5 V for QPEI/PVA/KOH as compared to 2.75 V for PEI/PVA/KOH) due to higher ionic conductivity (10 times more than PEI based SPE) and co-catalyzation effect of quaternized SPE. The other reason may be the difference in covalent bond formation (in carbamate) and ions-pair formation energy differences.

It is interesting to note (Figure 4) that increasing the applied voltage up to a certain extent increases the product formation. However, further increase in the applied voltage enhances the H_2 evolution whereas the product formation reduces. It is further course of study to find out the reason but the probable reason may be as follows; at significantly higher applied voltages the reaction kinetics were higher and more amount of water formed in anode due to anodic reaction as well as electroosmotic drag. It significantly imbalances water concentrations in the anode and cathode, which results in the diffusion of the water from anode to the cathode. Therefore, cathode catalyst layer floods with the water and the applied voltage is primarily used up for the hydrogen generation and the ERC hampers due to low solubility of gaseous CO_2 in the liquid water which is formed on the electrocatalyst. In addition to that the H_2 escapes from the reaction site and pushes back and dilute the incoming CO_2.

Based on the above discussion, it may be agreed that quaternary ammonium ion in the QPEI/PVA/KOH helps as a mediator or co-catalyst in the reduction of CO_2. It may also be suggested that electrostatically attracted quaternary ammonium ion of the QPEI/PVA/KOH to the negative cathode also assist the electron flow from cathode to CO_2 in the electrolysis. Once $CO_{2ads}^{\bullet -}$ is formed, the remaining reaction pathways to produce the products in the electroreduction of $CO_2$are proposed by several authors.[41-43] However, the pathway for the formation of C_2H_6 is not available. Therefore, the reaction pathway is being extended and proposed in the Figure 5C, in which the formation of C-C coupling might be formed through 2 molecules of $:CH_{3ads}$ to generate C_2H_6.

The cathode reactions for the different products are shown in the eq. (1-4) along with the standard half-cell potentials. The half-cell potential for the C_2H_6 formation was not available in the literature and thus standard calculation procedure (using bond strength, enthalpy change, Gibb's free energy change) was opted to find the standard half-cell potential.[44] It may be noted that the CH_4 and C_2H_6 have almost similar standard electrode potentials (E^o) and that may be the other probable reason that the one forms at the expense of other even when a slight change in the interface environment occur.

$$CO_{2(g)} + H_2O_{(l)} + 2e^- \rightarrow CO_{(g)} + 2OH^- \quad E^0 = -0.934 \text{ V} \quad (1)$$

$$CO_{2(g)} + 5H_2O_{(l)} + 6e^- \rightarrow CH_3OH_{(l)} + 6OH^- \quad E^0 = -0.812 \text{ V} \quad (2)$$

$$CO_{2(g)} + 6H_2O_{(l)} + 8e^- \rightarrow CH_{4(g)} + 8OH^- \quad E^0 = -0.659 \text{ V} \quad (3)$$

$$CO_{2(g)} + 10H_2O_{(l)} + 14e^- \rightarrow C_2H_{6(g)} + 14OH^- \quad E^0 = -0.685 \text{ V} \quad (4)$$

To quantify the preference of the product formation on others, selectivity was calculated for the CH_4 using PEI/PVA/KOH as SPE; CH_4 and C_2H_6 using QPEI/PVA/KOH as SPE at various applied voltages. Selectivity is defined as the amount of desired product to amount of total CO_2 reduction products obtained (based on the carbon content) during the reaction time of 25 min.[45] Maximum selectivity of 80% for CH_4 is obtained at 2.75V using PEI/PVA/KOH whereas, 77.3% for CH_4 at 2.5V in the case of QPEI/PVA/KOH. The Selectivity of C_2H_6 at 2.25V was 67.6% using QPEI/PVA/KOH, whereas the selectivity of CH_4 was reduced to around 16.4% as shown in table 1.

Table 1. Selectivity (%) of C_1 and C_2 products in dERC using SPEs during 25min.

	PEI/PVA/KOH	QPEI/PVA/KOH	
Voltage (V)	CH_4	CH_4	C_2H_6
1.8	19.6	19.9	0
2	37.4	64	10.6
2.25	68.4	16.4	67.6
2.5	65.8	77.3	0
2.75	80	60.18	0
3	41.2	39.19	0

It was observed that the quaternization has strong role on the evolution of CH_4, C_2H_6, and H_2. However, the other minor reaction products were hardly influenced. Faradaic efficiency was calculated for different ERC products obtained using PEI/PVA/KOH and QPEI/PVA/KOH after 25min of electrolysis at different voltages (Figure S4). Therefore, in order to further understand, Faradaic efficiency was evaluated for CH_4, C_2H_6, and H_2 (for different time intervals instead of only at the end of 25 min. duration) using PEI/PVA/KOH and QPEI/PVA/KOH and shown in the Figure 6. It may be noted that the voltage at which maximum product formation occur (using Figure 4) is used for the Figure 6. It can be seen that the Faradaic efficiency for CH_4 decreases, whereas Faradaic efficiency for H_2 increases at the

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same voltage using PEI/PVA/KOH at 2.75 V as the time increases. However, on comparing these results with the QPEI/PVA/KOH, it can be noted that after quaternization of the membrane, the Faradaic efficiency of CH_4 and C_2H_6 increases with the time or almost maintains the higher Faradaic efficiency as compared to its initial value at 5 min. The trend of the hydrogen Faradaic efficiency is also influenced by theQPEI/PVA/KOH SPE and reduced to 50% compared to PEI/PVA/KOH at all time intervals. The maximum Faradaic efficiency of C_2H_6 is 17% using QPEI/PVA/KOH SPE at 2.25V during 25min.

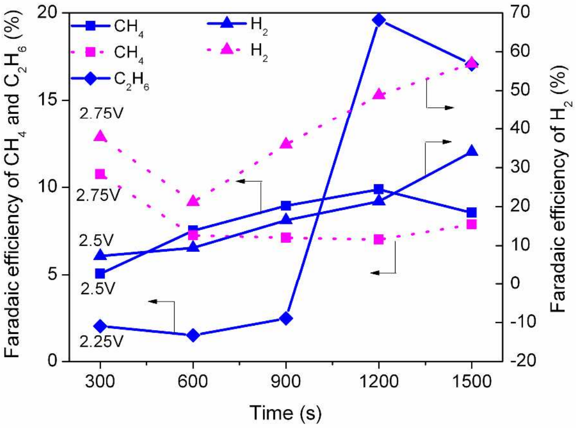

Figure 6. Faradaic efficiency of CH_4, and H_2 obtained as a function of time in the ERC using both SPEs and C_2H_6 for QPEI/PVA/KOH at the maximum selectivity. (Solid lines QPEI/PVA/KOH and dotted lines PEI/PVA/KOH)

Conclusions

Study on branched polyethylenimine (PEI) having amine groups as well as quaternized PEI (QPEI) was conducted to study the effect of these functional groups on the tuning of reaction zone. It was found that the hindered quaternary ammonium group in SPE has strong effect on the direct electrochemical reduction of gaseous CO_2 to the formation of C_2H_6. It was found that the QPEI/PVA/KOH SPE has great influence and on the reaction and it worked as a co-catalyst for the ERC. This study on the hindered quaternary bulky ammonium in the SPE was the first time in the application of dERC. It was interestingly found that under similar conditions the CH_4 was suppressed at a particular voltage and the C_2H_6 was formed only because of the fixed functional group. The $C_2H_6$was selectively formed with a Faradaic efficiency of 17% using QPEI/PVA/KOH over 25 min. duration. It clearly proved that SPE influences the system performance probably due to bulky propyl quaternary ammonium ion of the QPEI/PVA/KOH electrostatically attracted to the negative cathode thus assist the electron flow from cathode to CO_2 in the electrolysis. These studies suggest that hindered quaternary ammonium ions can promote CO_2 reduction in two ways: (1) these fixed functional group can create a suitable micro environment at the electrode; and (2) can mediate the electroreduction of CO_2. This study and the findings may open up research opportunities on solid electrolyte/polymer towards the sustainable generation of fuel generation, CO_2 reduction, and renewable energy storage.

Notes

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