Coupling Hydrogen Separation with Butanone Hydrogenation in an Electrochemical Hydrogen Pump with Sulfonated Poly (Phthalazinone Ether Sulfone Ketone) Membrane

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Abstract

This work reports the novel work of coupling H₂/CO₂ separation with biomass-derived butanone hydrogenation in non-fluorinated sulfonated poly (phthalazinone ether sulfone ketone) (SPPEsk) electrochemical hydrogen pump (EHP) reactor. Due to higher resistance to swelling, SPPEsk-based EHP reactor exhibits more excellent reaction rate in elevated temperature (60 °C) and higher butanone concentration (2M) as 270, 260 nmol cm⁻² s⁻¹, respectively, higher than 240, 200 nmol cm⁻² s⁻¹ of Nafion-based EHP reactors. Also, the SPPEsk-based EHP reactor remains 90% of initial hydrogenation rate after 4 batches, better than that of Nafion-based EHP reactors, which is only 62%. The energy efficiency of EHP separator reaches 40 % under H₂/CO₂ mixture feed mode, and electricity of about 0.3 kWh is consumed per Nm³ H₂ product, being superior to energy consumption compared with alternative processes like PSA and electrolysis of water. In addition, SPPEsk-based EHP exhibits better hydrogenation stability due to lower CO₂ permeation than Nafion. With increasing CO₂ content in H₂ feed, hydrogenation rate almost keeps constant at around 210 nmol cm⁻² s⁻¹ in SPPEsk-based EHP reactor while decreases fast to 50 nmol cm⁻²

s⁻¹ in Nafion/PTFE-based EHP reactor. These results show integration of gas separation with hydrogenation reactor is feasible in SPPEsk-based EHP reactor.

Keywords

Electrochemical hydrogen pump (EHP) • SPPEsk membrane • Hydrogenation • Hydrogen separation • Electrochemistry

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1. Introduction

Biomass is an abundant and environmentally friendly energy source that has the potential to replace diminishing fossil fuels and produce fuels and chemical products [1, 2]. In the conversion of cellulosic biomass into stable hydrocarbon fuels, hydrogenation of carbonyl groups in ketones, aldehydes and acids is considered to be an important step [3]. Hydrodeoxygenation of biomass-derived carbohydrates is also required to obtain desirable properties, such as high energy density and stability for combustion of liquid transportation fuels [4].

Conventionally, heterogeneous catalytic hydrogenation of ketones is implemented in three-phase reactors, e.g. batch autoclave slurry reactor with high pressure (~55 bar) and temperature (~433 K)[5] due to low solubility of hydrogen in the liquid reactants, which makes the dissociation of hydrogen on catalyst surface to be rate limiting step in the overall reaction. By contrast, electrocatalytic hydrogenation has the advantage of delivering in-situ atomic hydrogen to catalyst surface in a moderate, safe and efficient way without high pressure and turbulent mixing. A series of biomass-derived oxygenates have been hydrogenated in different types of electrocatalytic hydrogenation reactors, such as static single or two-chamber cells, and circulating single cell [6-8]. However, these processes always need a liquid supporting electrolyte, which is difficult to be separated from the products.

In order to address the issues of product separation and environmental pollution caused by liquid electrolytes, electrochemical hydrogen pump (EHP), with proton exchange membrane (PEM) as solid electrolyte, is proposed as an attractive

electrocatalytic hydrogenation reactor. As shown in Fig. 1, with power supply, hydrogen at the anode is electrochemically oxidized to produce protons, which transport across the PEM and are reduced to dissociated hydrogen atoms on the cathode catalyst surface and then get involved in hydrogenation with the adsorbed liquid reactant species. A variety of unsaturated organic compounds containing C=C [9-13], C=O [14-17] and S-S [18] bonds have been successfully hydrogenated in EHP reactors. For instance, Benziger[15] and Huber[16] selected acetone as the model compound of biomass derivatives, and investigated its hydrogenation with different catalysts and operating parameters [14,15]. We reported the great effects of hydrophobicity of diffusion layer on hydrogenation of different volatile reactants, i.e., butanone and maleic acid in aqueous solutions[19].

Fig. 1. Setup of the EHP separator & reactor for butanone hydrogenation with H₂/CO₂ (N₂) as anode feedstock. Temperature control is employed at the humidifier, anode inlet, EHP reactor and cathode circulating tank. a) Current collecting plate; b) Serpentine flow channel in graphite blocks; c) Microporous layer of GDL; d) Macroporous layer of GDL; e) Catalyst layer; f) Proton exchange membrane.

One of the unique features of EHP is the ability to separate hydrogen from H₂/CO₂[20,21], H₂/N₂[22,23], H₂/CH₄ [24] mixtures, which are major sources of hydrogen and widely derived from reformed gas, ammonia and methanol purges and various refinery tail gases. Compared with the state-of-the-art pressure-controlled

hydrogen production technologies, such as pressure swing adsorption (PSA), gas absorption and membrane separation [25], the EHP separator operates under atmospheric pressure with low operating costs, and can give high hydrogen purity (greater than 99 %). Hydrogen can also be produced from water electrolysis in EHP reactors, but it consumes too much electricity and is not economically competitive to the currently commercialized hydrogen production technologies. Since current methods of biomass conversion mostly require large quantities of pure hydrogen gas[26], the cost of hydrogen can be comparable to or much higher than that of biomass itself [15]. Consequently, it is urgent to develop an inexpensive method to produce hydrogen for biomass derivatives hydrogenation.

We herein report the coupling of hydrogen separation with biomass derivatives hydrogenation in an EHP reactor to make hydrogenation more convenient and efficient. In our previous work, Nafion/PTFE catalyst coated membrane (CCM) was used in EHP reactors to perform hydrogenation of butanone[19]. Although the hydrogenation rate was higher than that of the high-pressure catalytic hydrogenation, we observed damage of catalyst layer at high butanone concentration and long reaction time due to the high swelling ratio of Nafion in butanone and the product 2-butnaol. In comparison, non-fluorinated PEMs are more swelling resistant toward ketones and alcohols[27]; therefore, they have potential advantages over Nafion as membranes for EHP. We have proven the possibility of replacing Nafion with sulfonated poly (ether ether ketone)/crosslinked poly (acrylic acid) semi-interpenetrating polymer network membrane for H₂/CO₂ separation in an EHP, and obtained an energy efficiency

comparable to that of Nafion[28]. In the literature, high-temperature polybenzimidazole membranes were also investigated with H₂/CO₂/CO feedstock in an EHP separator to avoid CO poisoning to Pt catalyst at low temperatures[29,30]. To the best of our knowledge, there are few reports on non-fluorinated PEM-based EHP reactors to hydrogenate unsaturated organic compounds. In the present work, H₂/CO₂ separation is coupled with butanone hydrogenation into an EHP reactor. Different PEMs, e.g. SPPEsk (sulfonated poly (phthalazinone ether sulfone ketone) and Nafion-based membranes are investigated of their separation/hydrogenation performances, and are correlated to their proton conductivity, gas permeability and solvent swelling. Butanone is used as the model compound of biomass derivatives as in our previous work for comparison between different membranes. The potential advantages of SPPEsk as an alternative to Nafion membrane will be discussed in details.

2. Experimental

2.1 Materials

Butanone(99.5 %, Fisher), 2-butanol (99.5 %, Fisher), n-butanol (99.5 %, Fisher), N-methyl-2-pyrrolidone (NMP), fuming sulfuric acid (20-23 % SO₃), sulfuric acid (95-98%), hydrogen peroxide and other chemicals were obtained commercially and used without further purification. Nafion 115 and Nafion 212 were purchased from DuPont Co. Nafion/PTFE CCM was kindly provided by Sunrise Power Co., China with catalyst loading of 0.2 mg Pt cm⁻² at anode side and 0.4 mg Pt cm⁻² at cathode side[31,32]. Gas diffusion electrode was also provided by Sunrise Power Co. with

catalyst loading of 0.5 mg Pt cm⁻². Gas diffusion layer (GDL, 35BC) was kindly provided by SGL Tech. Germany; it consists of carbon paper with a micro-porous layer on one side.

Poly (phthalazinone ether sulfone ketone) (PPESK) with a sulfone/ketone ratio of 1:1 [33] was sulfonated according to our previous work[34]. In brief, PPESK was dissolved in the mixture of sulfuric acid and fuming sulfuric acid; the mixture was stirred with a magnetic stirrer at 60 °C for 2 h. The resulting SPPEsk was precipitated and washed with deionized water until neutral, and then vacuum-dried at 80 °C. SPPEsk membrane was prepared by solution casting method with NMP as the solvent; the dried membrane was treated with H₂SO₄ (3.0 M) solution for 12 h at room temperature, and then washed with deionized water to neutral.

2.2 Membrane characteristics

Ion exchange capacity (IEC) is the moles of sulfonic acid group per unit mass of dry membrane. It can be determined by ion exchange titration and calculated by equation (1), where C_{NaOH} and V_{NaOH} are the molar concentration and volume of NaOH solution, respectively; W_{dry} is the dry weight of SPPEsk.

$$IEC = \frac{C_{NaOH} V_{NaOH}}{W_{dry}} \quad (\text{mmol g}^{-1}) \quad (1)$$

Degree of sulfonation (DS) is determined by the same method to that of IEC and calculated by equation (2), where M_{PPESK} is the average molar mass of PPESK (434.5 g mol⁻¹), M_{SO₃H} is the molar mass of -SO₃H (81 g mol⁻¹).

$$DS = \frac{M_{PPESK} \cdot C_{NaOH} \cdot V_{NaOH}}{W_{dry} \cdot M_{SO_3H} \cdot C_{NaOH} \cdot V_{NaOH}} \quad (2)$$

Swelling ratio was calculated by comparing the dimensional changes of a

membrane sample before and after hydration at room temperature; its calculation follows equation (3), where L_{wet} and L_{dry} are the average length [$L_{wet} = (L_{wet1} \times L_{wet2})^{1/2}$, $L_{dry} = (L_{dry1} \times L_{dry2})^{1/2}$] of wet and dry samples, respectively. L_{wet1} , L_{wet2} , and L_{dry1} , L_{dry2} are the lengths and widths of wet membranes and dry membranes, respectively.

$$\text{Swelling ratio} = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \% \quad (3)$$

The in-plane proton conductivity (σ) was measured in water by four-electrode AC impedance method; its calculation was done according to equation (4), where L is the distance between the two electrodes, R is the resistance of the membrane, and S is the cross-sectional area of the membrane.

$$\sigma = \frac{L}{RS} \quad (4)$$

Hydrogen permeation across the membrane was evaluated by linear sweep voltammetry (LSV) [35] in the EHP with Ivium Technologies A08001 equipment. Sweep rate was 10 mV s^{-1} and the cell potential was scanned from 0 to 0.70 V. 50 mL min^{-1} hydrogen and 50 mL min^{-1} nitrogen were humidified and fed to the anode and cathode, respectively. Temperatures of both EHP and humidifier were set at 40°C . The permeated hydrogen across the membrane was indicated by a mass transport limiting current in the range of 0.15-0.70 V.

Dry CO_2 (or N_2) permeation coefficients in different dry membranes were tested using a home-made gas permeation cell with varied pressure and constant volume according to the literature[36]. Firstly, the membrane was mounted in the permeation cell, and the whole test system was degassed at room temperature. Then, the test gas

(CO₂ or N₂) was introduced from the upstream side, and the permanent pressure on the downstream side was monitored by a pressure transducer.

2.2 H₂/CO₂ separation and butanone hydrogenation

The schematic of the EHP separator & reactor is shown in Fig. 1. The EHP reactor has the same configuration as a proton exchange membrane fuel cell, which has serpentine flow channels with effective reaction area of 5.29 cm². MEAs with Nafion 212, Nafion 115 and SPPESEK membranes were made by sandwiching the membrane between two pieces of gas diffusion electrodes and hot-pressed at 140 °C, 3 MPa for 60 s.

H₂/CO₂ separation was investigated in the EHP, where the total dry flow rate of H₂/CO₂ at the anode was at 50 mL min⁻¹. Prior to the experiment startup, proportional amounts of H₂ and CO₂ were mixed (with CO₂ up to 75 vol. %), humidified, and then fed into the anode compartment. With an external potential applied (GWInSTEK GPD-3303S DC Power Supply), H₂ was oxidized to protons, which transported across the PEM and subsequently reduced to hydrogen gas again at the cathode. The steady-state voltage was measured by recording the voltage at a constant current for 0.5 h. The polarization curve was obtained by recording the cell voltage while increasing the current from 0.1 to 1.0 A (current density from 18.9 to 189.0 mA cm⁻²) at an increment step size of 0.1 A. The purity of hydrogen at cathode was analyzed by gas chromatography (GC-7890 TECHCOMP) equipped with a thermal conductivity detector (TCD-01 packed column). To eliminate the influence of oxygen and impurities, the cathode compartment was purged with nitrogen gas for about 0.5 h

before experiment. Hydrogen recovery and energy efficiency of the EHP separator can be calculated according to the equations (5) and (6)[21], where $\Delta H_{\text{combustion}}$ is the heat of combustion of hydrogen .

$$\text{Recovery efficiency} = \frac{i}{2F F_{\text{H}_2, \text{in}}^{\text{anode}}} \quad (5)$$

$$\text{Energy efficiency} = \frac{\frac{i}{2F} \Delta H_{\text{combustion}} - i V_{\text{applied}}}{F_{\text{H}_2, \text{in}}^{\text{anode}} \Delta H_{\text{combustion}}} \quad (6)$$

Butanone hydrogenation was performed with either pure H_2 (20 mL min⁻¹) or H_2/CO_2 (50 mL min⁻¹) as anode feedstock. 100 mL butanone aqueous solution was pumped into the cathode compartment with a circulating flow rate of 15 mL min⁻¹. At galvanostatic condition, certain amounts of protons transported across the PEM and were readily available for hydrogenation with the adsorbed butanone at cathode. Hydrogen evolution side reaction would occur due to the recombination of the excessive adsorbed hydrogen atoms, which may block the active sites of the cathode catalyst. The liquid product of butanone hydrogenation was analyzed by gas chromatography (FuLi® GC-9790II), equipped with a 10 % PEG-20000 packed column (3 m×3 mm) and a flame ionization detector. Quantitative n-butanol was added in the aqueous solution sample as internal standard substance. Hydrogenation rate (nmol cm⁻² s⁻¹) was the average value during the reaction time and on the basis of MEA geometric area. Current efficiency was defined by equation (7), where is the mol_{pro} is the mole number of the product, n is the number of electrons transferred, F is the Faraday constant (96485.34 C mol⁻¹), I_{cell} is the current observed in the experiment and Δt is the operational time.

$$\text{Current efficiency} = \frac{\text{mol}_{\text{pro}} n F}{I_{\text{cell}} \Delta t} \quad (7)$$

3. Results and Discussion

3.1 Hydrogenation of butanone in an EHP reactor with different PEMs and pure H₂ feedstock

Properties of different membranes are listed in Table 1. The main drawback of non-fluorinated membranes is their low proton conductivity as compared with Nafion membranes due to inadequate separation between hydrophilic and hydrophobic micro-phases[37]. Low proton conductivity will cause high ohmic polarization of fuel cell[28]. Here in the present work, proton conductivity of the SPPEsk and Nafion 115 membranes are compared; meanwhile, butanone hydrogenation rate with these two membranes is investigated to determine whether membrane conductivity is the rate limiting factor.

Fig. 2. Comparisons of: a) proton conductivity of the SPPEsk membranes with different DS and Nafion 115 at 40 °C; b) hydrogenation rate with SPPEsk and Nafion membranes as PEMs (56.7 mA cm⁻², 0.5 M butanone, 40 °C, 3h)

As shown in Fig. 2a, although proton conductivity of the SPPEsk increases with sulfonation degree (DS), it is much lower than that of Nafion 115. However, conductivity does not significantly influence the hydrogenation rate when DS is greater than 0.71 (EHP reactor with SPPEsk-0.31 (DS=0.31) could not run properly); Fig. 2b shows slight increase of butanone hydrogenation rate with DS,

Table 1. Electrochemical properties of different membranes (40 °C).					
PEMs	Dry Thickness (μm)	Wet Thickness (μm)	DS (mol %)	IEC (mmol g^{-1})	Conductivity (mS cm^{-1})
Nafion/PTFE [32,33]	20.0 $\pm$ 2.0	25.0	--	0.89	147.0 ^[a]
Nafion 212	50.8	60.0	--	0.92	112.3
Nafion 115	127.0	140.0	--	0.90	116.3
SPPEsk	~65.0	~70.0	0.71	1.43	33.8
[a] 25 °C in-plane conductivity.					

and the rate reaches almost the same level as that of Nafion 115. This is not surprising since the EHP reactor worked in a galvanostatic mode, where constant amount of protons transport across the membrane and membrane conductivity does not play much when the current is not high. In this case, a more meaningful comparison should be the applied potential to maintain a certain current density. It is seen from Fig. 2b that the relative low conductivity of SPPEsk membranes does not cause much increase of the applied potential of the SPPEsk-based EHP reactors as compared with the Nafion-based EHP reactors. Specifically, SPPEsk membrane with DS 0.71 (SPPEsk-0.71) is nearly 200 % lower in proton conductivity, but it caused only about 27 % increase in the applied potential as compared with Nafion 115. Applied potential indicates the overall resistance of the EHP reactor, which consists mainly of activation resistance, ohmic resistance and mass transport resistance. Benziger et al. suggested that the activation resistance of acetone and decene hydrogenation in EHP reactors was the rate-limiting resistance [14]. This agrees with our findings that ohmic resistance of SPPEsk is not the predominant reason for cell polarization.

SPPEsk-0.71- and Nafion-based EHP reactors were run at different conditions to further investigate their hydrogenation behaviors. In Fig. 3a, the SPPEsk -based EHP reactor gave hydrogenation rates that increased almost monotonically with reaction temperature, while the rates in the Nafion/PTFE-based EHP reactor exhibited a maximum and those in the Nafion 115-based EHP reactor show a plateau after a gradual growth. Meanwhile,

Fig. 3. Hydrogenation rate, conversion and current efficiency for hydrogenation of butanone to 2-butyl alcohol by using pure hydrogen gas in an EHP reactor as a function of: a) reactor temperature; b) butanone concentration; c) current density and d) reaction time. Reaction conditions for the SPPEsk and Nafion 115 based-EHP reactors: a)-d) 15 mL min^{-1} butanone, 20 mL min^{-1} H_2 ; a) 56.7 mA cm^{-2} , 0.5 M butanone, 3h, b) 56.7 mA cm^{-2} , 40 °C, 3h, c) 40 °C, 0.5 M butanone, 3h, and d) 56.7 mA cm^{-2} , 40 °C 0.5 M butanone. Data of the Nafion/PTFE based-EHP reactor derived from our previous work.^[19]

hydrogenation rates of butanone in SPPEsk-based EHP reactors can reach up to 270 $\text{nmol cm}^{-2} \text{s}^{-1}$ (32.4 $\text{mmol g}^{-1}_{\text{Pt}} \text{min}^{-1}$), much higher than that of the conventional hydrogenation at high pressure. The reaction rate of 12 $\text{mmol g}^{-1}_{\text{Pt}} \text{min}^{-1}$ was reported by Breen et al. with Pt/activated carbon (AC) as the catalyst at

3 bar and 30°C [38]. Different modes of rate variation with butanone concentration were also observed for the three membranes (Fig. 3b): the rate keeps increasing for the SPPEK-based EHP reactor, while decreases rapidly for Nafion/PTFE- and Nafion 115-based EHP reactors when butanone concentration is greater than 1.0 M. Fig. 3c shows increased conversion and hydrogenation rate while decreased current efficiency with current density, the latter is due to a side reaction involving recombination of excessive protons to produce H₂ (side reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) [16] As shown in Fig. 3d, the hydrogenation rate and current efficiency decrease, while the conversion increases with the reaction time, which will be explained later in this work.

Fig. 4. a) Swelling ratio of different membranes as a function of temperature in 0.5 M butanone and 2-butyl alcohol; b) Hydrogen crossover current density of different membranes at 40 °C.

The results in Fig. 3 indicate that SPPEK membrane is superior to Nafion-based membranes at higher temperature and butanone concentration. This is attributed to the different swelling and permeation properties of the membranes. Different from the membrane electrode assembly (MEA) in fuel cells, MEA of an EHP reactor is exposed to aqueous solutions of organic compounds at the cathode compartment; therefore, membrane normally suffers

from excessive swelling and harms the stability of MEA significantly. Fig. 4a shows the swelling ratio of the SPPEsk and Nafion 115 membranes in 0.5 M aqueous solutions of butanone and 2-butanol, respectively. Swelling ratio of the SPPEsk membrane is much lower than that of the Nafion 115, especially in 2-butanol solution, which means SPPEsk membrane has excellent solvent resistance. For Nafion/PTFE CCM, although swelling ratio of the Nafion/PTFE membrane itself is low (less than 5 %, not shown in Fig. 4, due to good solvent resistance of PTFE), the swelling of the Nafion binder causes the catalyst layer peeling off the Nafion/PTFE membrane [19]. As a result, hydrogenation rate decreased at high temperature ($>40\text{ }^{\circ}\text{C}$) and butanone concentration ($>1.0\text{ M}$) (Fig.3a, b). As compared with Nafion/PTFE CCM, hot pressing of Nafion 115 membrane with a gas diffusion electrode exhibits better hydrogenation stability at higher temperature and butanone concentration, but the higher swelling ratio of Nafion 115 in butanone and 2-butanol makes the Nafion 115-based EHP less stable than the SPPEsk-based one (Fig.3a, b).

In an EHP reactor, hydrogen can also permeate the membrane from anode to cathode as in fuel cells, which may block the contact between the liquid reactant and catalyst surface, and thus decrease hydrogenation rate. Hydrogen permeability of different membrane is investigated through the typical LSV in the EHP with H_2/N_2 as anode/cathode feedstock, respectively. As shown in Fig. 4b, the SPPEsk membrane exhibits lowest hydrogen crossover current density (0.38 mA cm^{-2}), which is even lower than that of Nafion115, the thickest of the

three membranes studied herein. These results indicate better hydrogen crossover resistance of the SPPEsk membrane, which is attributed to the tortuous pathway caused by its aromatic polymer backbone and lower solvent uptake.

Fig. 5. Stability test of butanone hydrogenation in EHP reactors with SPPEsk or Nafion/PTFE membrane (56.7 mA cm⁻², 0.5 M, 40 °C, 3 h for each batch)

It is seen from Fig. 3d that hydrogenation rate of the EHP reactor decreases with the reaction time. There are two possible reasons for this tendency: (1) product inhibition, that is, the produced 2-butanol may block the active sites of Pt catalyst due to competitive adsorption; (2) loss of catalytic activity, which could be caused by the damage of the catalyst layer with reaction proceeding. To further investigate the possible reasons, a stability test was performed by running the hydrogenation reaction with different membranes for four batches, and the results are shown in Fig. 5. For each batch, fresh butanone solution was circulated and the hydrogenation was kept for 3 h. For the SPPEsk-based EHP reactor, the hydrogenation rate slightly decreased during the repeated experiments, indicating that product inhibition is the

dominant reason for the decreased hydrogenation rate over prolonged reaction. Due to higher swelling of Nafion115 than SPPEsk, Nafion 115 based EHP reactor remains 84.3% of hydrogenation rate after 4 batches, slightly lower than that of the SPPEsk based EHP reactor. While for the Nafion/PTFE EHP reactor, about 37.8 % of the hydrogenation rate is lost after four batches; this observation, together with the observed peel-off of the catalyst layer from Nafion/PTFE membrane in our previous work[19], indicates the loss of catalytic activity. To minimize product inhibition and membrane swelling in 2-butanol, it is better to separate the product from the reaction mixture and then circulate the reactant back to the reactor. Further investigations of coupling hydrogenation with pervaporation separation are ongoing in our group.

From the above discussion, it is seen that Nafion-based membranes have evident shortcomings, which are related to their poor tolerance against ketone- and alcohol-containing biomass-derived feed stock. From this point of view, replacing Nafion-based membranes with non-fluorinated PEMs such as SPPEsk membrane is necessary to improve the efficiency and economy of biomass derivatives hydrogenation.

3.2 H₂/CO₂ separation in an EHP separator

High-purity hydrogen production is one of the unique features of the EHP separator. The EHP separator was run to investigate how fast hydrogen could be pumped through it with H₂/CO₂ anode feedstock. As shown in Table 2, even for 75 vol. % CO₂ in H₂ anode feedstock, hydrogen purity at the cathode is greater than 99 %

Table 2. Detection of H ₂ purity of cathode gas (56.7 mA cm ⁻² , 40 °C, 1atm, 75 vol. % CO ₂ in H ₂ anode feedstock).				
Gas	Composition (%)			
	SPPEsk-0.71	Nafion 115	Nafion 212	Nafion/PTFE
H ₂	>99.99	>99.99	99.79	99.25
CO ₂	<0.01	<0.01	0.21	0.75
The purity of H ₂ is detected by the gaseous part of the outlet stream.				

for all kinds of membranes. However, PEMs do influence purity of the hydrogen product. Using Nafion 115 or SPPEsk membranes as PEMs, hydrogen is recovered at the cathode with very high purity (>99.99 %), which is consistent with the findings of Benziger et al.[21] Hydrogen purity decreases with the decreasing thickness of the Nafion-based membranes. It is related to CO₂ permeation across the membranes, which may have negative effect on butanone hydrogenation as will be discussed later.

Fig. 6. Voltage–current density characteristics with different CO₂ content in H₂ at 40°C cell, 50 mL min⁻¹ anode inlet.

The most important controlling parameter in an EHP separator is the applied potential. It provides the driving force for hydrogen pumping. Fig. 6 shows the steady-state applied potential (averaged over 0.5 h) as a function of current density. For both the

Nafion/PTFE and SPPEsk membranes, the applied potential increases almost linearly with the current density, which indicates the ohmic resistance of the PEM is the rate-limiting factor[28]. At a certain current density, applied potential of the EHP separator with SPPEsk membrane is about 50 % higher than that with the Nafion/PTFE CCM; however, thickness of the SPPEsk membrane is three folds as compared with that of the Nafion/PTFE membrane (see Table 1). Therefore, the applied potential could be reduced through either decreasing the thickness or optimizing DS of the SPPEsk membrane. For both membranes, the overall resistances (slopes of the applied voltage over current density curves) increase gradually with the CO₂ content, the reason for which lies in the concentration polarization and poisoning effect of CO₂ as has been discussed in our previous work[39].

Fig. 7. Energy efficiency of the EHP separator as a function of hydrogen recovery with SPPEsk and Nafion/PTFE membrane, respectively. (40 °C, 50 mL min⁻¹ anode inlet).

Fig. 7 shows energy efficiency of the EHP separators as a function of hydrogen recovery using Nafion/PTFE and SPPEsk membranes, respectively.

Energy efficiency of the SPPEsk-based EHP separator is about 35 % at 60 %

hydrogen recovery, which is 80 % of that achieved with the Nafion/PTFE EHP separator (43.5 %). Higher energy efficiency (over 90 %) and hydrogen recovery (over 90 %) can be further achieved by reducing the hydrogen feed flow per unit area of MEA or by multistage operation [21,40]. Although H_2/CO_2 flow rate of the present EHP separators needs to be optimized, it consumes much less electricity as compared with the state-of-the-art hydrogen producing technologies such as PSA[42], membrane separation[42] and water electrolysis. For a rough comparison by Unisim Design (R400) simulation, considering a H_2/CO_2 mixture (25 vol. % H_2 , 1 atm) compressed to 2 MPa before entering PSA or membrane separation equipment; 1 Nm^3 hydrogen product consumes roughly 0.5 kWh electricity for compressor by Unisim Design (R400) simulation, while only ca. 0.3 kWh is consumed per Nm^3 H_2 using Nafion-based EHP and 0.44 kWh is consumed by SPPEK-based EHP separation technology in this study. Although SPPEK-based EHP separation consumes more energy than Nafion-based EHP separator, it still cost less when compared with PSA method. In addition, the results in this paper are calculated at low hydrogen pressure, EHP separator would exhibit greater advantages in energy consumption to gain high pressure hydrogen. Additionally, the applied potential of running an EHP H_2/CO_2 separator is also much lower than that of the water electrolysis (higher than 1.23 V). Therefore, incorporation of H_2/CO_2 separation into the EHP reactor is superior to pure H_2 or H_2O as anode feedstock in the energy perspective. Furthermore, the EHP acts as both H_2/CO_2 separator and

hydrogenation reactor in the present work, which can avoid the large capital for hydrogen product as in the state-of-the-art hydrogen producing technologies.

3.3 Coupling of H₂/CO₂ separation with butanone hydrogenation in an EHP

When the hydrogen feed for EHP reactor is supplied from a H₂/CO₂ mixture, decrease of hydrogenation rate is investigated even though galvanostatic mode is used to keep a constant current density for each batch. As shown in Fig. 8a, with increasing CO₂ content, butanone hydrogenation rate decreases in the Nafion-based EHP reactors, and it drops most rapidly in the Nafion/PTFE-based EHP reactor, while almost keeps constant in the SPPEsk-based EHP reactor. Although hydrogenation rate of the SPPEsk-based EHP reactor is slightly lower than that of the Nafion 115-based EHP reactor for pure H₂ feedstock, it becomes higher when CO₂ content exceeds 75 vol. %, indicating better stability and superior properties of the SPPEsk-based EHP reactor in case of low hydrogen content in the anode feedstock.

Fig. 8. Butanone hydrogenation rates using different PEMs as a function of: a) CO₂ content in H₂/CO₂ anode feedstock; b) N₂ content in H₂/N₂ anode feedstock (40 °C, 0.5 M, 56.7 mA cm⁻², 3 h).

With increasing CO₂ content, hydrogenation behaviors of SPPEsk and Nafion-based EHP reactors are supposed to be related to different CO₂ permeability, which may cause concentration polarization and poisoning effects. Table 3 lists CO₂

permeability coefficients of different membranes. For the Nafion-based membranes, permeability coefficient of CO₂ increases with the decrease of membrane thickness, which agrees with the hydrogenation rate drop profile exhibited in Fig. 8a. With the thinnest Nafion/PTFE composite membrane, more CO₂ would permeate the membrane from anode to cathode, which may block the contact of the liquid reactant with the catalyst surface (i.e. concentration polarization effect) or poison the Pt catalyst. Compared with Nafion/PTFE and Nafion 212, SPPEsk exhibits excellent performance in blocking CO₂. Although the permeation of CO₂ across the SPPEsk membrane is slightly higher than that across Nafion 115 the difference should be negligible if taking membrane thickness into account (Nafion 115 (127 μm) is almost twice as thick as SPPEsk membrane (70 μm)). Note that all the permeability tests were conducted with dry gas and dry membrane. Considering several times higher swelling ratio of Nafion 115 in butanone and 2-butanol (shown in Fig. 4a), the better hydrogenation rate of SPPEsk membrane working with feed of higher CO₂ content should be attributed to the combined effect of lower permeability and lower swelling.

Table 3. Permeability coefficient of dry CO ₂ and N ₂ of different dry membranes.				
Permeability coefficient	PEMs			
	Nafion/PTFE	Nafion 212	Nafion 115	SPPEsk-0.71
P _{CO₂} (GPU*10 ²)	21.17	5.10	2.10	3.47
P _{N₂} (GPU*10 ²)	7.36	0.68	0.27	0.10
ΔP=0.15 MPa, T=298.15 K, 1GPU=3.35×10 ⁻¹⁰ mol m ⁻² s ⁻¹ Pa ⁻¹				

Poisoning effect of CO₂ on anode Pt catalyst has been widely investigated for hydrogen oxidation at anode of fuel cells[43] and EHP separators[20]. We have shown that CO₂ reduced active surface of anode Pt catalyst in an EHP separator

through cyclic voltammetry investigation [44]. Bruijin et al.[44] and Bellows et al.[45] proposed that CO would be generated through water gas shift reaction (eq.8 and 9), which subsequently poisons Pt catalyst and undermines the hydrogen oxidation reaction.

By contrast, there is quite limited information in the literature concerning whether permeated CO₂ poisons the cathode catalyst. To gain an understanding on this, hydrogenation rate with H₂/CO₂ anode feedstock is compared with that of H₂/N₂. Different from the behavior with H₂/CO₂ anode feedstock, hydrogenation rate almost keeps constant for all the membranes with the increasing N₂ content in H₂/N₂(Fig. 8b). N₂ can also permeate across the PEMs (see Table 3) although the permeation coefficient is lower than that of CO₂ [46]. Since N₂ is an inert gas, it would not poison Pt catalyst; it only causes mass transport resistance [22]. And the concentration polarization effect shows its influence on hydrogenation rate only at high N₂ content (greater than 75 vol. % in Fig. 8b). Therefore, the different hydrogenation behaviors with H₂/CO₂ or H₂/N₂ anode feedstock suggests that poisoning of the cathode Pt catalyst by the permeated CO₂ across the PEM is a main reason for the decreased hydrogenation rate with H₂/CO₂ feedstock. It is essential for PEMs to possess low CO₂ permeability in order to keep good stability of the EHP reactor.

4. Conclusion

The present work investigates the possibility of coupling H₂/CO₂ separation with

biomass-derived butanone hydrogenation in an EHP, and replacing Nafion with non-fluorinated SPPEsk membrane. Butanone hydrogenation rates for both Nafion- and SPPEsk-based EHP reactors are comparable and achieve up to $270 \text{ nmol cm}^{-2} \text{ s}^{-1}$ much higher than that of the conventional hydrogenation at high pressure. Hydrogenation rate in the SPPEsk-based EHP reactor with pure H_2 feedstock increases with temperature and butanone concentration; it becomes higher than that of the Nafion-based EHP reactors at 60°C and 2 M due to less swelling of the SPPEsk membrane in butanone and 2-butanol solutions (both aqueous). In the membrane EHP separator with H_2/CO_2 feedstock, hydrogen is recovered with high purity ($>99\%$), and the purity is greater than 99.99% for SPPEsk-based one. Energy efficiency of the SPPEsk-based EHP separator is about 20% lower than that of the Nafion/PTFE-based EHP separator, reaching 35% at hydrogen recovery of 60% . Interactions are observed as H_2/CO_2 separation is coupled with butanone hydrogenation in the EHP. Lower CO_2 permeability of the SPPEsk membrane leads to less poisoning of the cathode Pt catalyst; as a result, butanone hydrogenation rate almost keeps constant in SPPEsk-based EHP reactor with the increasing CO_2 content in H_2 , while decreases fast in the Nafion-based EHP reactors. A rough comparison on electricity consumption of gas compression suggests that incorporation of H_2/CO_2 separation into EHP reactor is superior to pure H_2 or H_2O as anode feedstock in the energy perspective. Therefore, it is essential for PEM to possess low CO_2 permeability and solvent swelling in order to keep good stability of such an EHP separator & reactor.

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