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## Introduction

Many current methods of biomass conversion require the use of high quantities of hydrogen gas. This usage of hydrogen gas constitutes a large fraction of the overall operating cost of these technologies.<sup>1–4</sup> An example is the hydrodeoxygenation of carbohydrates, vegetable oils, and pyrolysis oils, which can require up to 0.12 kg H<sub>2</sub> per kg feedstock.<sup>5–8</sup> The cost of hydrogen gas is about \$1 per kg near hydrogen pipelines, but can increase 10 times or more when storage and transportation are required.<sup>9</sup> This is especially important in remote locations, where biomass is plentiful and inexpensive. Assuming \$2 per kg H<sub>2</sub>, the cost of the hydrogen gas feedstock could be as high

# The electrocatalytic hydrogenation of furanic compounds in a continuous electrocatalytic membrane reactor†

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The electrocatalytic hydrogenation of biomass derived oxygenates in a continuous electrocatalytic membrane reactor presents a promising method of fuel and chemical production that minimizes usage of solvents and has the potential to be powered using renewable electricity. In this paper we demonstrate the use of a continuous-flow electrocatalytic membrane reactor for the reduction of aqueous solutions of furfural into furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF). Protons needed for hydrogenation were obtained from the electrolysis of water at the anode of the reactor. Pd was identified as the most active monometallic catalyst of 5 different catalysts tested for the hydrogenation of aqueous furfural with hydrogen gas in a high-throughput reactor. Thus Pd/C was tested as a cathode catalyst for the electrocatalytic hydrogenation of furfural. At a power input of 0.1W, Pd/C was 4.4 times more active (per active metal site) as a cathode catalyst in the electrocatalytic hydrogenation of furfural than Pt/C. The main products for the electrocatalytic hydrogenation of furfural were FA (54–100% selectivity) and THFA (0–26% selectivity). MF and MTHF were also detected in selectivities of 8%. Varying the reactor temperature between 30 °C and 70 °C had a minimal effect on reaction rate for furfural conversion. Using hydrogen gas at the anode, in place of water electrolysis, produced slightly higher rates of product formation at a lower power input. Sparging hydrogen gas on the cathode had no effect on reaction rate or selectivity, and was used to examine the addition of recycling loops to the continuous electrocatalytic membrane reactor.

as \$0.13 per gallon diesel fuel for hydrodeoxygenation (HDO) of vegetable oils and \$1.00 per gallon of gasoline for the HDO of bio-oils and sugars.<sup>5–8</sup> These costs amount to a significant portion of the overall price of the product. This example illustrates the need for methods of biomass conversion that minimize consumption of hydrogen gas.

We recently demonstrated that proton exchange membrane (PEM) technology can be used to electrocatalytically hydrogenate acetone to isopropyl alcohol (IPA) using protons generated from the electrolysis of water.<sup>10</sup> Water electrolysis requires an electrical power input (defined as the product of applied voltage and measured current). The required cell potential for water electrolysis is proportional to the Gibbs free energy *via* the number of electrons transferred and Faraday's constant ( $\Delta G = -nFE_{Cell}$ ). Cell current has a complicated relationship with cell potential, which was simplified by Datta into a model based on charge balances, mass balances, and Butler–Volmer kinetics.<sup>11</sup>

The electrocatalytic hydrogenation of biomass-derived oxygenates has several key advantages over other methods of biomass conversion. The most significant advantage is that no hydrogen gas is required. This is especially important in

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remote locations where hydrogen gas is expensive.9 Another advantage is that this technology stores electricity as a liquid transportation fuel that fits into existing infrastructure.<sup>12,13</sup> This technology could thus be used for electricity storage, especially when the electricity is generated from renewable sources like wind turbines.<sup>14</sup> Compared to the fermentation of glucose to ethanol, the electrocatalytic HDO of glucose to hexane in a continuous electrocatalytic membrane reactor has the potential to produce 50% more energy as a liquid fuel.<sup>10</sup> HDO of biomass produces a wide range of products including alcohols, polyols, and alkanes that can be used for fuel blendstocks or sold into the commodity chemicals market.5,15,16 Thus PEM technology could be used to produce a wide range of products from the electrocatalytic hydrogenation of biomass-derived molecules. Both the anodic water electrolysis and the cathodic biomass hydrogenation take place in one single continuous reactor that could easily be scaled up to a commercial level. Having one single reactor vessel could reduce the capital cost of a facility for biomass conversion. The simplicity of the reactor design would also decrease the operating costs. Finally, one of the most important advantages of electrocatalysis compared to conventional catalysis is the ability to manipulate the size of the activation barrier by controlling the electrode potential.<sup>17,18</sup> Therefore, reactions that require high temperatures and pressures in a conventional catalytic system (e.g., hydrolysis of water) will readily occur at atmospheric temperatures and pressures in the continuous electrocatalytic membrane reactor due to the application of a voltage.<sup>19,20</sup> Additionally, controlling the electrode potential has the ability to affect reaction selectivity, as high potentials may promote the formation of secondary or side-products. Based on the required power input, electrocatalytic hydrogenation in a continuous electrocatalytic membrane reactor will be most economically profitable when hydrogen gas is expensive and electricity is cheap.

Furfural is a, commercially relevant, platform molecule that can produce a wide range of products by hydrogenation reactions (Fig. 1) and shows significant potential for electrocatalytic hydrogenation.<sup>1,21–24</sup> Products from furfural hydrogenation include furfuryl alcohol (FA), tetrahydrofurfuryl alcohol



Fig. 1 Reaction scheme for the hydrogenation of furfural.

(THFA), 2-methylfuran (MF), and 2-methyltetrahydrofuran (MTHF). Furfural is produced from the acid-catalyzed dehydration of xylose at around 300 000 metric tons per year, and cannot be used directly as a fuel due to its tendency to polymerize at room temperatures.<sup>21</sup> However, MTHF has an octane number of 74 and can be blended into p-series gasoline fuel.<sup>1,22</sup> Additionally, THFA is a "green" solvent used in industrial applications such as biocides and pesticides, coatings and dyes, and stripping formulations.<sup>25</sup> The Gibbs's free energies and standard cell potentials for the electrocatalytic formation of these products from furfural are presented in Table 1. As mentioned above, reactions using protons generated from water electrolysis require a higher cell potential, and thus a greater power input. The formation of THFA and MF from FA requires 1.01 V and 1.09 V, respectively. This indicates that hydrogenating the furan ring to form THFA is marginally more favorable than hydrogenolysis of the conjugated hydroxyl group to form MF. Similarly, hydrogenating the furan ring in MF to form MTHF (1.5 V) is more favorable than hydrogenolysis of the non-conjugated hydroxyl group in THFA to form MTHF (2.06 V). In fact, though MTHF can be produced from THFA in conventional catalysis, this route is highly unlikely to occur electrocatalytically because the formation of hydrogen gas, requiring 1.23 V, is significantly more thermodynamically favorable and, subsequently, faster.

Several catalysts have been studied as replacements for the toxic copper chromate catalyst historically used for furfural hydrogenation. These catalysts include: carbon supported copper,<sup>26,27</sup> a copper/iron catalyst,<sup>28</sup> RANEY® Ni,<sup>29</sup> and monometallic and bimetallic Pt, Pd, Sn, and Ru.<sup>25,30-33</sup> These catalysts can also be employed in electrocatalysis. Miller, Jackson, and Saffron explored furfural hydrogenation to FA and MF in an undivided electrochemical cell using a sacrificial Ni or Ni-Fe alloy anode with an Al, Fe, Ni, or Cu cathode, and an ammonium chloride electrolyte.<sup>34</sup> FA production was favored at pH of 5.0 while MF production was favored at pH 1.0. Increasing the current density decreased the reaction rate and efficiency. Chu et al. demonstrated the electrocatalytic hydrogenation of furfural using a nanoporous TiO<sub>2</sub> catalyst with enhanced surface area in an ionic liquid.<sup>35</sup> Belgsir has investigated the electrocatalytic conversion of furfural using both a flow-through reactor and a half-cell batch reactor.36,37 In the flow-through reactor, the oxidation of furfural to furonic acid over a nickel modified graphite felt electrode was coupled with

 Table 1
 Gibbs free energy and standard cell potentials for the hydrogenation of furfural using hydrogen gas and water electrolysis

|  | Hydrogen gas                         |   | Water electrolysis                   |   |
|--|--------------------------------------|---|--------------------------------------|---|
| Reaction   | $\Delta G (\text{kJ mol}^{-1})$      | $E_{\text{cell}}\left(\mathbf{V}\right)$                              | $\Delta G (\text{kJ mol}^{-1})$      | $E_{\text{cell}}(\mathbf{V})$             |
| 1. Furfural $\rightarrow$ FA<br>2. FA $\rightarrow$ THFA<br>3. FA $\rightarrow$ MF<br>4. MF $\rightarrow$ MTHF<br>5. THEA $\rightarrow$ MTHF | -35.95<br>-80.97<br>-25.27<br>104.78 | $\begin{array}{c} 0.19 \\ 0.21 \\ 0.13 \\ -0.27 \\ -0.83 \end{array}$ | 200.38<br>391.69<br>211.06<br>577.44 | -1.04<br>-1.01<br>-1.09<br>-1.50<br>-2.06 |

the reduction of furfural to furfuryl alcohol over a copper modified graphite felt cathode.<sup>36</sup> Oxidation took place in a 1 M NaCl + NaOH + LiOH anolyte and reduction in a phosphate buffer ( $H_3PO_4$  + NaOH, pH 6.6) catholyte. In the half-cell reactor, the electrocatalytic hydrogenation of furfural was studied on Au, Pt, Ni, Cu, and Pb electrodes in different acidic and basic media.<sup>37</sup> It was determined that Cu was active towards furfural conversion and that the highest conversion was achieved in a basic solution.

From an economic viewpoint it would be desirable to do the electrocatalytic hydrogenation of furfural in a continuous flow reactor using stable electrodes without the use of a liquid electrolyte. Previous work has suggested that hydrogenation is most favorable in a basic media;<sup>37</sup> however the Nafion membrane used in PEM fuel cells is acidic. The environment in the membrane electrode assembly (MEA) therefore limits the types of metal catalysts that can be used for hydrogenation without degradation. In this paper we will study the electrocatalytic hydrogenation of 5 wt% furfural and 5 wt% furfuryl alcohol in water in a continuous electrocatalytic membrane reactor with an MEA consisting of an acidic Nafion polymer electrolyte, Pt– Ru/C anode, and Pd/C or Pt/C cathodes.

#### Experimental

The following chemicals were used in this study: furfural  $(C_5H_4O_2, 99\%$  Acros Organics), furfuryl alcohol  $(C_5H_6O_2, 98\%$  Acros Organics), tetrahydrofurfuryl alcohol  $(C_5H_1O_2, 99\%$  Acros Organics), 2-methylfuran  $(C_5H_6O, 99\%$  Acros Organics), and 2-methyltetrahydrofuran  $(C_5H_{10}O, 99\%$  Acros Organics). Liquid samples were analyzed by an Agilent 7890A gas chromatography system, equipped with an RTX-VMS capillary column and a flame ionization detector (FID). Helium was used as the carrier gas with a column flow rate of 30 ml min<sup>-1</sup>. One  $\mu$ l liquid sample was injected for each analysis. Carbon balances were closed with 89  $\pm$  2.5% for all experiments reported here.

#### **Electrocatalytic experiments**

The schematic for the continuous electrocatalytic membrane reactor system, including the feedstocks and products, is shown in Fig. 2. Membrane electrode assemblies (MEAs) were fabricated using 4.0 mg cm<sup>-2</sup> Pt-Ru/C anodes and 1.0 mg cm<sup>-2</sup> Pd/C or Pt/C cathodes. The working electrode used for half-cell experiments was 1.0 mg cm<sup>-2</sup> Pd/C. Catalyst ink solutions consisted of 40 wt% Pt-Ru/C, 20 wt% Pd/C, or 20 wt% Pt/C (ETEK) mixed with deionized water, liquid Nafion ionomer (Ion Power, Inc. Dupont DE520 Nafion ® Solution), and 1-propanol (99% Fisher). The ink solution was deposited on teflonized carbon paper (Toray, TGPH-090) using a spray technique. MEAs were made using a hot-press at 140 °C and 1500 psi for 3 minutes. The membrane was Nafion 115 from Nara Cell-Tech. The electrochemically active surface area of the cathodes was measured as 44.7  $m^2\ g^{-1}$  and 48.2  $m^2\ g^{-1}$  for Pd/C and Pt/C, respectively. These measurements were taken



Fig. 2 Continuous electrocatalytic membrane reactor schematic for the electrocatalytic hydrogenation of furfural over Pd/C or Pt/C using protons derived from the electrolysis of water over Pt–Ru/C.

using cyclic voltammetry conducted in an electrochemical half-cell reactor using 20 wt% carbon supported metal at a loading of 1.0 mg cm<sup>-2</sup>. The CVs were recorded within the potential range of -0.2 to 1.0 V ( $\nu$ s. Ag/AgCl) at a scan rate of 50 mV s<sup>-1</sup>.

Continuous electrocatalytic membrane reactor experiments were conducted using a PEM fuel cell (http://www.fuelcelltechnologies.com) with a 5 cm<sup>2</sup> surface area. Serpentine flow channels for the anode and cathode were set in graphite blocks, and liquid flow rates were controlled by Eldex® Optos Metering Pumps. Water, at a flow of 0.6 ml min<sup>-1</sup>, or 60 sccm humidified hydrogen gas were used at the anode of the continuous electrocatalytic membrane reactor. The cathode contained either 5 wt% furfural, 5 wt% furfuryl alcohol, or 5 wt% furfural sparged with 30 sccm hydrogen gas. The liquid flow rate at the cathode was  $0.2 \text{ ml min}^{-1}$ . The cathode residence time at this flow rate was approximately 20 minutes. The electrocatalytic reactor was purged with the anode and cathode feeds for 20 minutes prior to applying a voltage to ensure the cell was fully saturated with fresh feedstock. Samples were collected from the cathode after an additional 20 minutes of flow or once the current had reached steady-state. Gas samples at the cathode outlet were collected by sparging the liquid product with N2. Voltage application and current measurements were performed with a Metrohm Autolab Potentiostat, PGSTAT302N, coupled with a 10 Amp Current Booster, BSTR10A. Gas samples were analyzed by a GC-5890 Hewlett Packard gas chromatography system equipped with a packed column and a thermal conductivity detector (TCD). Nitrogen was used as the carrier gas with a column pressure of 47 psi.

Electrocatalytic half-cell experiments, for the purpose of determining active surface area of the catalyst, were conducted using a standard three-electrode set-up. A platinum wire and Ag/AgCl electrode served respectively as the counter and reference electrodes. The catalyst ink solution for the working electrode was made in the same manner as described above. The reaction solution was 5 wt% furfural in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The half-cell was capped to maintain an oxygen-free environment, and



Fig. 3 Comparison of initial TOFs over different monometallic catalysts for (a) the APH of furfural at 100 °C and 800 psia for 75 minutes with 4.8 wt% furfural solution as feedstock, and (b) the APH of furfuryl alcohol at 80 °C and 800 psia for 3 hours with 4.8 wt% FA solution as feedstock.

the solution was purged with  $N_2$  for 10 minutes prior to introducing  $H_2$  at a flow rate of 20 sccm. Gases were flowed into the half-cell through a glass frit and the solution was stirred throughout the reaction to ensure adequate mixing.

#### High-throughput reactor (HTR) experiments

Monometallic catalysts were prepared by the incipient wetness impregnation method with the following metal precursors:  $[Pt(NH_3)_4](NO_3)_2,$  $Ru(NO)(NO_3)_3$  $[Pd(NH_3)_4](NO_3)_2$ , and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Strem Chemicals Inc.). The 5 wt% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst was purchased from Strem Chemicals Inc. Gammaalumina (y-Al<sub>2</sub>O<sub>3</sub>) was employed as a support, formed from Boehmite (Sasol) pretreated in a conventional oven at 600 °C for 4 hours. The catalysts were reduced under H<sub>2</sub> flow at 300 °C for Pd, Pt, Ru, and Rh and 400 °C for Ni for 2 hours and purged with He flow for 30 minutes. After reduction, the catalysts were cooled down to room temperature under He flow, then sealed, and stored in a glove box. The metal dispersions of the prepared catalysts were determined by H<sub>2</sub> chemisorption using a Quantachrome Autosorb iQ Automated Gas Sorption system. Before chemisorption, all catalysts were reduced in situ under H<sub>2</sub> flow up to 300 °C (Pd, Pt, Ru and Rh) and 400 °C (Ni) with a heating rate of rate 1 °C min<sup>-1</sup>, held for 2 hours, purged with He for 2 hours, evacuated for 140 minutes, and cooled to room temperature.

The aqueous-phase hydrogenation (APH) of furfural and FA was conducted using a HTR (HEL Group CAT24) consisting of 24 wells machined into a high-pressure stainless steel cylindrical chamber. The temperature, pressure, and stirring speed were controlled and monitored by WinIso E670 system software. Prior to the reaction, 5–10 mg of catalyst was loaded into a glass tube reactor placed on the HTR wells in the glove box and the catalysts were reduced under  $H_2$  flow at 200 °C for 12 hours in case re-oxidation occurs. After reduction, the catalysts were cooled down to room temperature under He flow, then sealed, and moved to the glove box. In the glove box, magnetic stir bars and 2 ml of 4.8 wt% furfural and FA

solutions were loaded into glass tube reactors containing reduced catalysts. The HTR was then sealed with closed valves and transported to the reactor system bench. The HTR was first pressurized to 650 psia and then heated to 100 °C for the APH of furfural and 80 °C for the APH of FA at a rate of 20 °C min<sup>-1</sup>, after which it was pressurized to a final pressure of 800 psia. The temperature and pressure were kept constant during the reaction, and a stirring speed of 800 rpm was used. Once a reaction set finished, the HTR was cooled down to room temperature at a rate of 14 °C min<sup>-1</sup>. The HTR was then depressurized to atmospheric pressure, and samples from each well are taken and filtered at 0.2 microns.

#### Results

#### Catalyst selection

The initial activity of different alumina supported monometallic catalysts including Pd, Pt, Ru, Rh, and Ni for the APH of furfural and FA was investigated. Fig. 3 shows the comparison of initial turnover frequencies (TOFs) for the APH of furfural and FA according to catalyst type. The initial activity for the APH of furfural decreased as follows: Pd > Ni > Ru > Pt > Rh (at 100 °C). The initial TOF of the 3 wt% Pd catalyst was 7.5 times higher than the initial TOF of the 3 wt% Pt catalyst for the APH of furfural. The order of initial activity for the APH of FA followed: Pd > Ni > Ru > Rh ~ Pt (at 80 °C). The 1 wt% Pd catalyst exhibited the highest initial TOF, which was 15.3 times as high as the initial TOF of the 1 wt% Pt catalyst. Ni also showed a high initial activity for the APH of furfural and FA. However, Ni catalysts have been reported to solubilize in acidic environments and thus Ni is not a suitable monometallic PEM catalyst.<sup>38</sup> Although Pt had a low activity for furfural and FA hydrogenation, it was investigated further using the continuous electrocatalytic membrane reactor due to its popularity as both a fuel cell catalyst and as a conventional catalyst for furfural hydrogenation. 32,33,39,40

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**Fig. 4** Current density and power input as a function of applied voltage for the electrocatalytic hydrogenation of furfural to form furfuryl alcohol and tetrahydro-furfuryl alcohol over (a) Pd/C and (b) Pt/C. Reaction conditions: 30 °C, cathode: 111.7  $h^{-1}$  WHSV furfural over 1.0 mg cm<sup>-2</sup> Pd/C or Pt/C, anode: H<sub>2</sub>O at 0.6 ml min<sup>-1</sup> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C.



Fig. 5 (a) Rate of furfural conversion and (b) current efficiency as a function of power input for the electrocatalytic hydrogenation of furfural. Reaction conditions: 30 °C, anode:  $H_2O$  at 0.6 ml min<sup>-1</sup> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C, cathode: 111.7 h<sup>-1</sup> WHSV furfural over 1.0 mg cm<sup>-2</sup> Pd/C or 1.0 mg cm<sup>-2</sup> Pt/C.

The electrocatalytic hydrogenation of aqueous solutions of 5 wt% furfural in a continuous electrocatalytic membrane reactor was investigated using both Pd/C and Pt/C cathodes, as shown in Fig. 4 and 5. Fig. 4 shows the relationship between current density and power input as a function of applied voltage for the (a) Pd/C and (b) Pt/C cathode catalysts. The power input is defined as the product of the applied voltage and the measured system current. The weight hourly space velocity (WHSV), defined as the ratio of the mass flow of furfural to the mass of the metal catalyst present in the MEA, was held constant for both of the catalytic systems. Both the current density and the power input are slightly higher for Pt/ C than for Pd/C. This shows that the Pt/C catalyst has a higher electrochemically active surface area and lower overpotential than Pd/C.<sup>41</sup> The higher current density produced by Pt/C translates directly to a higher flux of protons, using Faraday's constant, as compared to Pd/C.

The current efficiency at a given power input is up to 50 times higher for Pd/C compared to Pt/C as shown in Fig. 5a. The current efficiency is the ratio of current contributing to furfural hydrogenation divided by the overall current. Current

that does not contribute to furfural hydrogenation instead produces hydrogen gas (that is not used to hydrogenate furfural) at the cathode. The high current efficiency for the Pd/C catalyst indicates that Pd/C is a better catalyst than Pt/C for furfural conversion, while Pt/C is a better catalyst for producing hydrogen gas. This is further demonstrated in Fig. 5b, which depicts the rate of furfural conversion as a function of power input. The rate of furfural conversion is up to 5 times higher with the Pd/C catalyst as compared to the Pt/C catalyst. Additionally, furfural hydrogenation over Pd/C at a power input of 0.05 W or more produced FA, THFA, MF, and MTHF. However, no MF or MTHF was detected from furfural hydrogenation over Pt/C (results not shown). THFA was only present at a power input of 0.3 W. Based on the higher rate of furfural conversion and higher current efficiency, Pd/C was used as the cathode catalyst for all additional experiments.

#### Effect of applied voltage

The effect of applied voltage on the electrocatalytic hydrogenation of furfural using a Pd/C cathode was investigated over a voltage range of 1.15 V to 1.75 V. The results for current



Fig. 6 Selectivity as a function of (a) conversion and (b) applied voltage for the electrocatalytic hydrogenation of furfural over Pd/C. Reaction conditions: 30 °C, cathode: 111.7 h<sup>-1</sup> WHSV furfural over 1.0 mg cm<sup>-2</sup> Pd/C, anode: H<sub>3</sub>O at 0.6 ml min<sup>-1</sup> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C.

efficiency (Fig. 5a) and reaction rate (Fig. 5b) are presented as a function of total power input. The current efficiency ranged from 24-30%. This signifies that 70-76% of the current contributed to the evolution of hydrogen gas, rather than the hydrogenation of furfural. Liquid product selectivity is reported as a function of conversion in Fig. 6a and as a function of applied voltage in Fig. 6b. FA was the main product with 100% selectivity at low conversion and applied voltage. This result was expected given the theoretical standard cell potential values in Table 1. As furfural conversion increased, the FA selectivity decreased and other products were observed. As shown in Table 1, a cell potential of 1.04 V is required for converting furfural to FA, which is below the applied voltages of 1.15 and 1.3 V. Converting FA to THFA or MF requires 1.01 and 1.09 V respectively. However, at low conversion there is only low quantities of FA present and these products are not observed. As conversion increases to 2%, THFA, MF, and MTHF are detected at selectivities of 8-10%. Increasing the applied voltage to 1.75 V increases conversion to 6% under the reaction conditions used in this study. At this voltage, THFA was the second most abundant product with a selectivity of 26%. MF and MTHF remain at 8% selectivity. The high selectivity for THFA, as compared to MF or MTHF, was expected based on the thermodynamic calculations. The high standard cell potential (2.06 V) for THFA hydrogenation to MTHF is consistent with these experimental results and indicates that the main route for formation of MTHF is through MF.

Fig. 7 compares the rate of hydrogen production, furfural conversion, and hydrogen production plus furfural conversion ("combined rate") as a function of power input for two different systems: (1)  $H_2O$  on the anode/furfural on the cathode ( $H_2O$ -furfural system); and (2)  $H_2O$  on the anode/ hydrated  $N_2$  on the cathode ( $H_2O$ - $N_2$  system). Hydrogen gas was collected at the cathode by sparging the liquid product with nitrogen gas. The highest measured rate of hydrogen production was from the  $H_2O$ - $N_2$  system. At power inputs less than 0.05 W, the rate of hydrogen production was comparable for both systems. However, as the power input increases, the



Fig. 7 Reaction rate as a function of power input. Reaction conditions: 30 °C, cathode: 111.7  $h^{-1}$  WHSV furfural or 60 sccm N<sub>2</sub> over 1.0 mg cm<sup>-2</sup> Pd/C, anode: H<sub>2</sub>O at 0.6 ml min<sup>-1</sup> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C.

rate of hydrogen production for the H<sub>2</sub>O-furfural system decreased compared to the rate of hydrogen production for the H<sub>2</sub>O-N<sub>2</sub> system. The rate of furfural conversion in the H<sub>2</sub>O-furfural system increased with increasing power input, but is up to 16 times lower than the rate of hydrogen production in the same system. Also shown in Fig. 7 is the rate of hydrogen production plus the rate of furfural conversion for the H<sub>2</sub>Ofurfural system. This "combined rate" is similar to the rate of hydrogen production in the H2O-N2 system, especially for power inputs below 0.1 W. Thus, it can be inferred that, at power inputs below 0.1 W, the furfural does not inhibit the rate of water electrolysis. The difference between hydrogen production in the H2O-N2 system and the "combined rate" in the H2O-furfural system increases with increasing power input. This difference coincides with a decrease in the current density of the H<sub>2</sub>O-furfural system. One possible cause could be that the liquid furfural feedstock at the cathode of the H2O-furfural system results in a higher over potential, and thus a lower current, than the gaseous N<sub>2</sub> in the  $H_2O-N_2$  system.

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**Fig. 8** (a) Current density, current efficiency and (b) furfural conversion rate, power input as a function of temperature for the electrocatalytic hydrogenation of furfural. Reaction conditions: 1.45 V, cathode: 111.7 h<sup>-1</sup> WHSV furfural over 1.0 mg cm<sup>-2</sup> Pd/C, anode: H<sub>2</sub>O at 0.6 ml min<sup>-1</sup> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C.



**Fig. 9** (a) Reactant concentration as a function of applied voltage and (b) reactant conversion rate as a function of power input for the electrocatalytic hydrogenation of furfuryl alcohol. Furfural conversion is included in Fig. 9b for the purpose of comparison. Reaction conditions: 30 °C, cathode: 111.7 h<sup>-1</sup> WHSV furfuryl alcohol (or 111.7 h<sup>-1</sup> WHSV furfural) over 1.0 mg cm<sup>-2</sup> Pd/C, anode: H<sub>2</sub>O at 0.6 ml min<sup>-1</sup> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C.

#### Effect of reactor temperature

The temperature of the continuous electrocatalytic membrane reactor was increased from 30 °C to 70 °C to investigate the effect of reaction temperature. Fig. 8a shows that the current density increases while the current efficiency decreases, with increasing temperature. The decreasing current efficiency signifies an increase in the production of hydrogen gas. These results indicate that the increase in temperature promotes water electrolysis and production of hydrogen gas but not furfural hydrogenation. This is confirmed by Fig. 8b, which shows no change in the furfural conversion rate, despite the increase in power input. There is also no statistically significant change in liquid product selectivity as the temperature increases (results not shown). In non-electrocatalytic systems furfural hydrogenation is generally conducted at temperatures greater than 120 °C.<sup>41</sup> The Nafion membrane used in the continuous electrocatalytic membrane reactor is only stable up to 80 °C, and therefore, additional experiments could be conducted using a high temperature membrane, such as a Celtec®P membrane from BASF, or a high temperature fuel cell to further increase temperature and study its effects on reaction rate and efficiency.<sup>42,43</sup>

#### Electrocatalytic hydrogenation of furfuryl alcohol

Fig. 9 depicts results from the electrocatalytic hydrogenation of FA. Fig. 6 shows that at low conversion and low applied voltage only FA was produced for furfural conversion. It was explained that sufficient voltage was applied for producing MF and THFA but that insufficient FA was present for these reactions. At higher voltages, where there was a higher degree of furfural conversion, MF and THFA were produced. Given this explanation, the electrocatalytic reduction of FA should produce MF and THFA at an applied voltage of 1.15 V. This is confirmed by the results in Fig. 9a, which show that MF and THFA are produced at approximately 3.8 mM at an applied voltage of 1.15 V. However, at 1.15 V no MTHF is observed, likely because there is insufficient MF present for further reaction. FA conversion and concentrations of THFA and MTHF increase as applied voltage increases. However, the concentration of MF increases from 1.15 V to 1.45 V, but then

decreases when voltage is increased to 1.75 V. This trend appears to further confirm that MF is an intermetidate for MTHF, as was discussed for Fig. 6b.

The FA conversion rate increased with increasing power input, as shown in Fig. 9b. Initially, the rate of FA conversion is higher than the rate of furfural conversion. Furfural hydrogenation produces primarily FA at low power input, which involves only hydrogenating the aldehyde functionality. FA hydrogenation produces THFA, which involves hydrogenating the furan ring, and MF, which involves hydrogenolysis of the hydroxyl group. Therefore, the rate of hydrogenating the aldehyde functionality in furfural appears lower than the sum of the rates of hydrogenating the furan ring and hydrogenolysis of the hydroxyl group in FA. At power inputs greater than 0.12 W, the rate of furfural conversion is higher than the rate of FA conversion. This result indicates that the rate of furfural conversion increases due to the added reactions of FA to THFA, FA to MF, and MF to MTHF.

#### Electrocatalytic hydrogenation using hydrogen gas

The rate of furfural hydrogenation at low power input using protons derived from hydrogen gas (the H<sub>2</sub>-furfural system) was found to be comparable to the rate of furfural hydrogenation at higher power input using protons derived from water electrolysis (the H<sub>2</sub>O-furfural system), as shown in Fig. 10. This is similar to results obtained for the electrocatalytic hydrogenation of acetone.<sup>10</sup> Fig. 10 also shows that the H<sub>2</sub>-furfural system has a lower current efficiency, at all investigated power inputs, as compared to the H<sub>2</sub>O-furfural system. Therefore, the H2-furfural system not only has a higher rate of furfural conversion but also a higher rate of hydrogen gas production. Both systems have comparable liquid product selectivities of MF and MTHF. Selectivity of THFA is slightly higher in the H<sub>2</sub>-furfural system and selectivity of FA is slightly lower in the H<sub>2</sub>-furfural system, as compared to the H<sub>2</sub>O-furfural system (see ESI<sup>†</sup>).



**Fig. 10** Current efficiency (CE) and furfural conversion rate as a function of power input for the electrocatalytic hydrogenation of furfural using hydrogen gas or water at the anode. Reaction conditions: 30 °C, cathode: 111.7  $h^{-1}$  WHSV furfural over 1.0 mg cm<sup>-2</sup> Pd/C, anode: H<sub>2</sub>O at 0.6 ml min<sup>-1</sup> or 30 sccm H<sub>2</sub> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C.

#### Discussion

The main challenge in electrocatalytic hydrogenation using a continuous electrocatalytic membrane reactor is that a large fraction of the current goes towards generating hydrogen gas that is not used in the hydrogenation reaction. Thus, to make this system more practical is highly desirable to increase the rate of hydrogen consumption due to hydrogenation reactions over the rate of hydrogen gas evolution. This is based not only on the low rate of furfural hydrogenation (0.6 moles furfural per moles Pd min), but also the low current efficiency (24-30%), which indicates that the majority of protons are going towards hydrogen gas evolution. One method of increasing the furfural hydrogenation rate is to increase the applied voltage, which equates to an increase in power input. However, this also increases the rate of hydrogen evolution and thereby affects the efficiency of the reactor. It was shown in Fig. 6b that current efficiency for furfural conversion is between 24-30%, and increases with increasing power input. Power efficiency is defined as the sum of the higher heating value of the hydrogenated products divided by the sum of the higher heating value of the reactants plus the electrical power input. Fig. 11 shows that there is an initial drop in power efficiency as a function of power input, followed by a graduate decrease at inputs greater than 0.05 W. Therefore, a small decrease in current or power efficiency may be a worthwhile penalty for a higher rate of furfural hydrogenation. However, the applied voltage also affects selectivity, and thus increasing it may increase overall reaction rate but not promote the desired product (ex. FA at 1.3 V vs. FA at 1.75 V as seen in Fig. 6). One method of manipulating applied voltage without influencing selectivity is to change the species being oxidized at the anode. For example, Rodriguez-Rivera et al. found that the rate of cathodic hydrogen gas evolution is comparable for oxidation of an aqueous solution of polyoxometalates (POM), which occurs at ~0.62 V, as compared to oxidation of water at  $\sim$ 2.0 V.<sup>44</sup>



Fig. 11 Power efficiency as a function of power input for the electrocatalytic hydrogenation of furfural. Reaction conditions: 30 °C, cathode: 111.7  $h^{-1}$  WHSV furfural over 1.0 mg cm<sup>-2</sup> Pd/C, anode: H<sub>2</sub>O at 0.6 ml min<sup>-1</sup> over 4.0 mg cm<sup>-2</sup> Pt–Ru/C.

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**Fig. 12** Reactor schematics for the hydrogenation of furfural using protons generated from water electrolysis. (a) PEM water electrolyzer coupled with a conventional catalytic reactor. Hydrogen gas is produced from water electrolysis in the PEM electrolyzer, which is then used in a conventional catalytic reactor to hydrogenate furfural. (b) Single continuous electrocatalytic membrane reactor with second catalytic bed (electrocatalytic or conventional catalytic) and recycle loops.

A second method of increasing the rate of furfural hydrogenation is to increase the reactor temperature. However, the temperature of the continuous electrocatalytic membrane reactor is limited by the Nafion membrane and, as discussed earlier, either a high temperature membrane or another type of fuel cell is required to achieve temperatures over 80 °C.42,43 Additionally, increasing reactor temperature was seen to decrease current efficiency (Fig. 8a). A third option to increase reaction rate is to change the catalyst or its support. Ni, Fe, and Cu have been used for electrocatalytic furfural hydrogenation and shown high conversion and selectivity to FA, despite leaching of these metals.<sup>34</sup> These metals could be readily incorporated into an MEA for an alkaline fuel cell. Using conventional catalysis, it has been shown that Pt/titania results in higher selectivity to FA and THFA while Pt/silica and Pt/magnesia have higher selectivity towards MF, 2-pentanol, and 2pentanone.32 Extensive research has been conducted on improving the kinetics for  $H_2/O_2$  fuel cells, which could be applicable to electrocatalysis of biomass derived molecules. Research to improve oxygen reduction reactions (ORR) has examined Pt monolayers on Au, Rh, Pd, Ru, and Ir supports as well as monolayers of Pt-M (M = Ir, Ru, Rh, Pd, Au, Re, or Os) deposited on the surfaces of Pd (111) single crystal or carbon supported Pd nanoparticles.45,46 To decrease CO poisoning and improve reaction kinetics at the anode, Pt alloys such as PtRu, PtMo, and PtSn have been examined.47,48 An added difficulty in choosing the proper catalyst is that the catalyst represents a large portion of the cost of the overall process.49,50 The aforementioned Pt monolayers drastically decrease the amount, and therefore, cost of Pt in the catalyst. Even cheaper substrates made from tungsten carbide, have also been found to have a similar hydrogen binding energy and activity to bulk Pt, when only a Pt monolayer is present.51,52

Alternate reactor designs could also be used for this process, as shown in Fig. 12. One of the most basic methods of hydrogenating furfural would be to produce hydrogen in a PEM electrolyzer and then use the hydrogen in a conventional catalytic reactor, as seen in Fig. 12a. The disadvantage of this design is that the hydrogenation of furfural requires highpressure hydrogen. Therefore a compressor would be needed to recompress the hydrogen gas after reaction. In addition, this approach requires a separate high-pressure reactor. The continuous electrocatalytic membrane reactor proposed in this study was depicted in Fig. 2. In this design, water is electrolyzed at the anode of the electrocatalytic reactor and the generated protons are used to reduce furfural at the cathode. The benefit of this design, as compared to that shown in Fig. 12a, is that it does not require pressurization, storage, or transport of hydrogen gas and takes place all in one reactor, thereby minimizing energy and materials usage.

The continuous electrocatalytic membrane reactor could be further developed to recycle hydrogen and/or furfural from the cathodic product stream and/or to include a second catalytic bed to further hydrogenate remaining furfural (Fig. 12b). The second catalytic bed could be conventional, and thus require a compressor, or electrocatalytic. A recycle loop for water exiting the anode could also be incorporated. The purpose of recycling hydrogen gas in the cathode feedstock is not only to conserve resources but also to increase the rate of furfural hydrogenation. However, experiments conducted with hydrogen gas sparged at the cathode inlet showed no statistically relevant changes in furfural conversion rate or product selectivity (see ESI<sup>†</sup>).

### Conclusion

In this paper we studied the electrocatalytic hydrogenation of furfural in a continuous electrocatalytic membrane reactor using protons derived from water electrolysis. Pd was 7.5 times more active than Pt for hydrogenation of furfural in a batch reactor. Consistent with the batch reactor experiments, Pd/C was 4.4 times more active than Pt/C for hydrogenation of furfural at the cathode of the continuous electrocatalytic membrane reactor. Identified products from furfural hydrogenation over Pd/C were FA, THFA, MF, and MTHF. The product selectivity changed as a function of applied voltage. The FA selectivity decreased and the THFA selectivity increased with increasing voltage. Selectivity towards MF and MTHF was 8% at power inputs over 0.02 W. The current efficiency was 24–30%, which indicates that up to 76% of the overall current contributed towards the evolution of hydrogen gas instead of furfural hydrogenation. Adjusting the temperature between 30–70 °C was not found to affect the rate of furfural conversion. The electrocatalytic hydrogenation of FA resulted in high selectivities of THFA and MF, and a faster initial rate of conversion than furfural hydrogenation. Using hydrogen gas as the source of protons instead of water electrolysis resulted in a comparable rate of furfural conversion at a lower power input. Sparging hydrogen gas at the cathode had no statistically significant effect on the reaction rate.

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