



Short communication

Clean hydrogen production from methanol–water solutions via power-saved electrolytic reforming process

Sunghyun Uhm^{a,*}, Hongrae Jeon^b, Tae Jin Kim^c, Jaeyoung Lee^{a,b,**}^a Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju 500-712, Republic of Korea^b Electrochemical Reaction and Technology Laboratory, SESE, GIST, Gwangju 500-712, Republic of Korea^c Catalyst & Process R&D Center, SK Innovation, Daejeon 305-712, Republic of Korea

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ABSTRACT

We report the highly power-saved electrolytic hydrogen production by electrochemical reforming of methanol–water solutions. Operating conditions are optimized in terms of current efficiency, the stability of electrocatalysts and methanol loss. Energy requirements are also compared with conventional water electrolysis. It has been observed that current efficiency of methanol electrolysis increases with current density, while decreasing with cell temperature. Pt is found to be more effective electrocatalyst for methanol electrolysis in comparison with PtRu since current efficiency and overvoltage in conjunction with stability against dissolution should be taken into account. At high current density of 300 mA cm⁻², methanol electrolysis can save more than 65% electrical energy necessary to produce 1 kg of hydrogen compared with water electrolysis.

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1. Introduction

As hydrogen release via water electrolysis promises to be of great future importance, scientific efforts are oriented to the improvement of the electrolytic process efficiency. The most commonly used commercial water electrolyzers are based on the alkaline or proton exchange membrane (PEM) technology. The cost of hydrogen produced in this manner is largely determined by the cost of electrical energy expended. The energy requirement to produce hydrogen by the water electrolysis is in turn governed by the operating voltage, a quantity determined by the thermodynamic potential for water electrolysis and the efficiency of the process. For water electrolysis, the operating voltage is typically over 1.4 V even in the most efficient electrolyzer [1–3]. If this operating voltage is lowered, the energy requirements can be reduced dramatically and correspondingly the cost of hydrogen production.

From this standpoint, the replacement of water at the anode side with organic molecules can be used to produce clean H₂ which can be utilized in other systems, resulting in an improvement in the overall system performance. Such an electrochemical reforming or electrolysis has been demonstrated using several different

sources [4–10]. Botte et al. have reported that the electrooxidation of aqueous ammonia on PtIr catalysts in alkaline electrolyzer allows for the production of high purity hydrogen at cell voltages as low as 0.36 V [4,5]. Recently several studies including a patent by Narayanan et al. have focused on H₂ production by electrolysis of methanol–water solutions [6–8]. They have dealt with various parameters to be considered for methanol electrolysis. In fact, the standard potential for the methanol oxidation is only –0.016 V (vs. SHE) compared to 1.23 V for the water oxidation. It has been estimated that H₂ production from methanol electrolysis costs about 50% less compared to that of water, even when the cost of methanol is taken into account [6].

In this paper, we report results obtained for methanol electrolysis to optimize the operating conditions with respect to current efficiency, methanol loss, and which is more effective electrocatalyst. Also, the energy consumption of methanol electrolysis are evaluated and compared with that of water electrolysis under given conditions.

2. Experimental

The chemicals used in this study were PtRu and Pt black (Johnson Matthey), isopropyl alcohol and methanol (Junsei), 5% Nafion solution (1100EW, DuPont) and Millipore water (18.2 MΩ). The catalyst inks were prepared by dispersing the catalyst nanoparticles into appropriate amounts of water, 5% Nafion ionomer solution and isopropyl alcohol. Pt black (3 mg cm⁻²) and PtRu black were used as

* Corresponding author. Tel.: +82 62 715 2571; fax: +82 62 715 2434.

** Corresponding author at: Ertl Center for Electrochemistry and Catalysis, GIST, Gwangju 500-712, Republic of Korea. Tel.: +82 62 715 2571; fax: +82 62 715 2434.

E-mail addresses: laminat@hanmail.net (S. Uhm), Jaeyoung@gist.ac.kr (J. Lee).

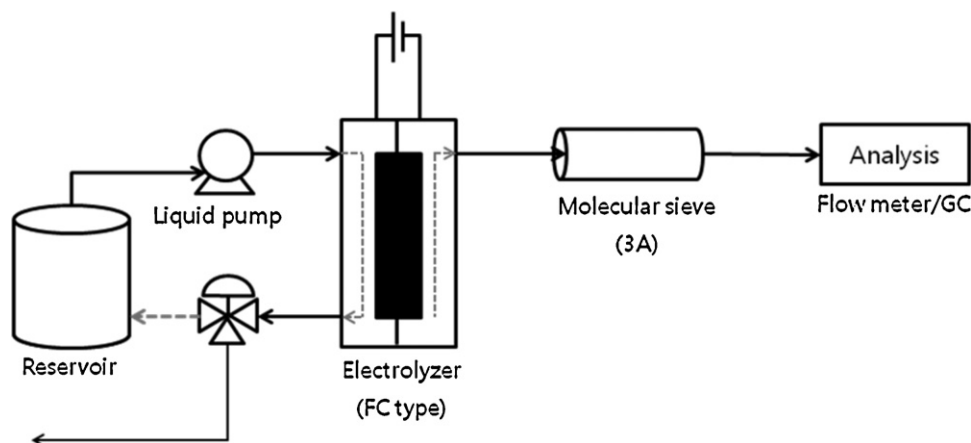


Fig. 1. Schematic illustration of methanol–water electrolysis.

anode catalysts, and Pt black (3 mg cm^{-2}) was used as cathode catalyst, respectively. Then both the anode and cathode catalyst inks were sprayed onto respective diffusion media. Anode and cathode diffusion media were SGL 25AA and SGL 35BC, respectively. SGL 25AA is the plain carbon paper without any hydrophobic agent such as Teflon for better diffusion of methanol. On the other hand, SGL 35BC is 5% teflonized carbon paper with microporous layer for easy removal of produced hydrogen. The membrane electrode assemblies (MEAs) were constructed in a way that as-prepared anodes and cathode electrodes were placed on either side of a Nafion 115

membrane. The assembly was hot-pressed at 10 MPa for 5 min at 140°C .

The as-prepared MEA, with an electrode area of 9 cm^2 , was sandwiched between two graphite blocks having serpentine flow path channels. The cell temperature was increased from 30°C to 70°C and the concentration of methanol–water solutions was also varied from 0.5 M to 2 M. The electrolysis was performed by connecting the anode of the cell to the working electrode and the cathode to the reference and counter electrodes of the potentiostat (Autolab PGSTAT30, Eco Chemie), respectively. All electrolysis

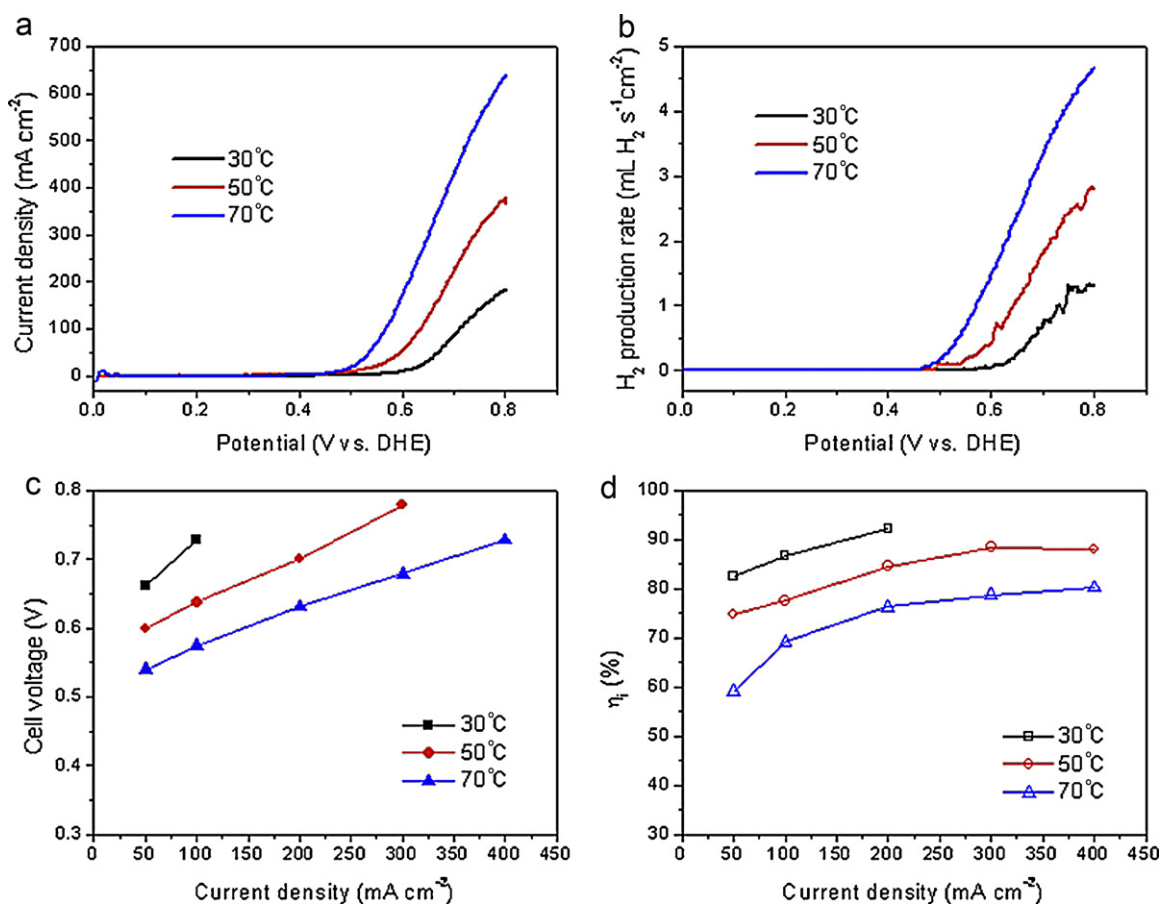


Fig. 2. Current variation as a function of applied potential with 1.0 M methanol at a scan rate of 5 mV s^{-1} (a) and corresponding hydrogen production rate (b) with respect to cell temperature. Cell voltage variation as a function of applied current (c) and corresponding current efficiency (d).

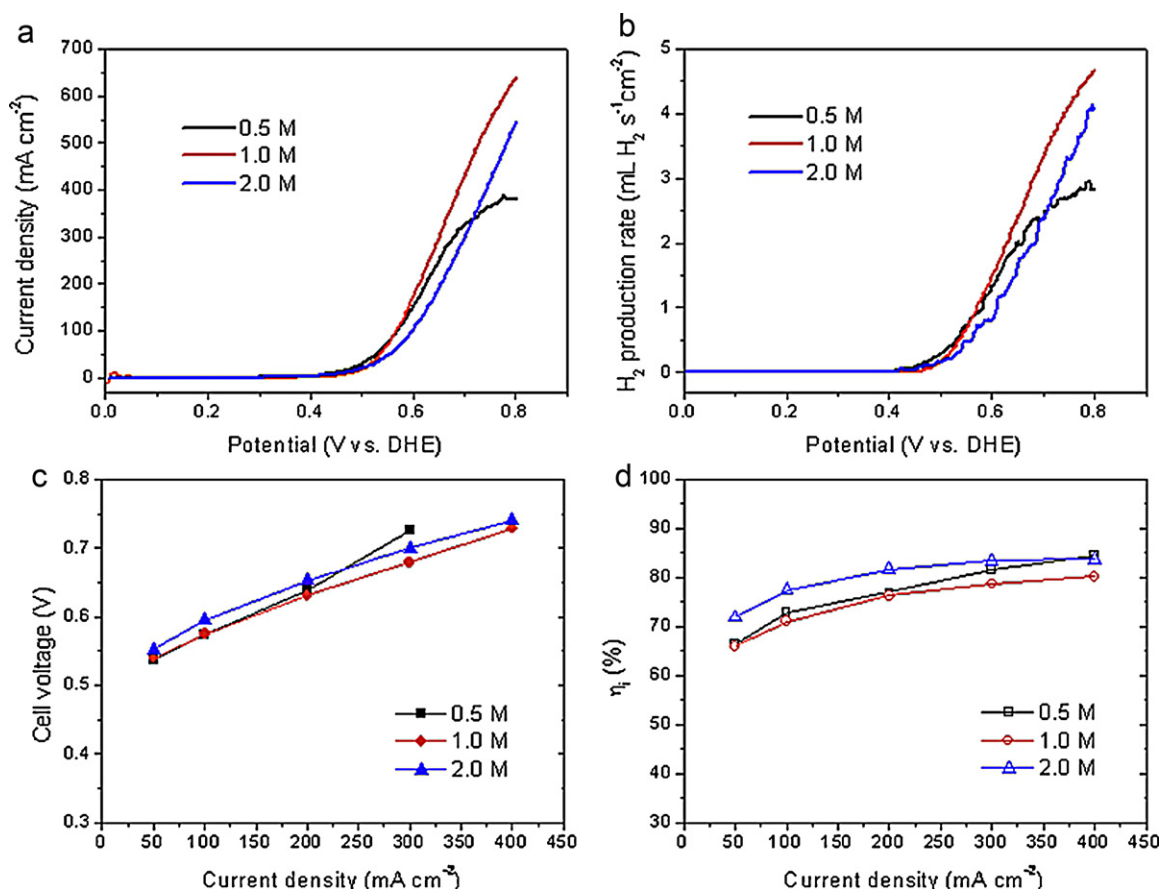


Fig. 3. Current variation as a function of applied potential at a scan rate of 5 mV s^{-1} (a) and corresponding hydrogen production rate (b) with respect to methanol concentration. Cell voltage variation as a function of applied current (c) and corresponding current efficiency (d). All experiments were carried out at 70°C .

experiments were first conducted in the potential-controlled mode by way of hydrogen production in a cathode as a dynamic hydrogen electrode (DHE), assuming that there is only a few dozens of overvoltage. And then, cell voltage was measured in the galvanostatic, current-controlled mode to evaluate the energy consumption and stability. At every measurement, high frequency resistance was also obtained with milliohmmeter (Hioki 3560 AC Milliohm HiTester). The flow rate of the cathode-exhaust gas was measured using a gas flow meter (Agilent Flowmeter ADM2000) after the cathode-exhaust passed through a molecular sieve as shown in Fig. 1. The cathode exhaust gas was also analyzed by gas chromatography.

3. Results and discussion

A set of experiments were carried out to study of effects of cell temperature and methanol concentration on the methanol electrolysis. It can be seen in Fig. 2 that current density increases with cell temperature. This is as expected, since both methanol oxidation kinetics and hydrogen production rate improve as cell temperature increases. Current efficiency, however, decreases with an increase of cell temperature as shown in Fig. 2(d). This is due largely to the mechanism of methanol electrooxidation on Pt-based catalysts. First, a sequence of dehydrogenation steps give rise to adsorbed methanolic residues at low overpotential. In the absence of a promoting element, water discharge occurs at high anodic overpotentials on Pt with the formation of Pt–OH species at the catalyst surface. The final step is the reaction of Pt–OH groups with neighboring methanolic residues to give carbon dioxide [11,12]. Therefore, the higher the overpotential is, the more abundant Pt–OH species becomes, enabling methanolic residues

to proceed further toward carbon dioxide. This complete reaction generating six electrons is shown to give higher current efficiency, whereas higher overvoltage requires much more energy necessary to produce equivalent hydrogen. This is in good agreement with the fact that the current efficiency increases with an increase of current density as shown in Fig. 2(d). However, the current efficiency does not increase any more at more than 300 mA cm^{-2} . Note that the increased temperature higher than 70°C is expected to give rise to dramatic increase of methanol and water crossover through membrane, resulting in the significant loss of methanol [13].

Fig. 3 shows the dependence of cell voltage and current efficiency on the methanol concentration in feed solutions. The results shown in Fig. 3(a) are very similar to those in normal direct methanol fuel cell anode, except that the effect of methanol crossover is not significant due to absence of air as an oxidant in the cathode side. Instead, 2 M methanol gave rise to higher overpotential because hygroscopic property of methanol can readily adsorb water molecules in polymer electrolyte as well as in the catalyst layers, leading to the decrease of ionic conductivity that is proven by measuring the gradual increase of high frequency resistance. This behavior becomes more probable in our experimental conditions since the plain carbon paper is used as an anode diffusion media to promote the methanol diffusion even at low temperature as well as low methanol concentration.

It has been shown that the alloying of Ru with Pt enables us to synthesize electrocatalysts which strongly promote the oxidation of both methanol and CO. Based on the bifunctional mechanism [14], Pt-sites adsorb methanol through a dehydrogenation step whereas the alloying element, namely Ru, adsorbs oxygenated species from water. The methanolic residues adsorbed on Pt sites

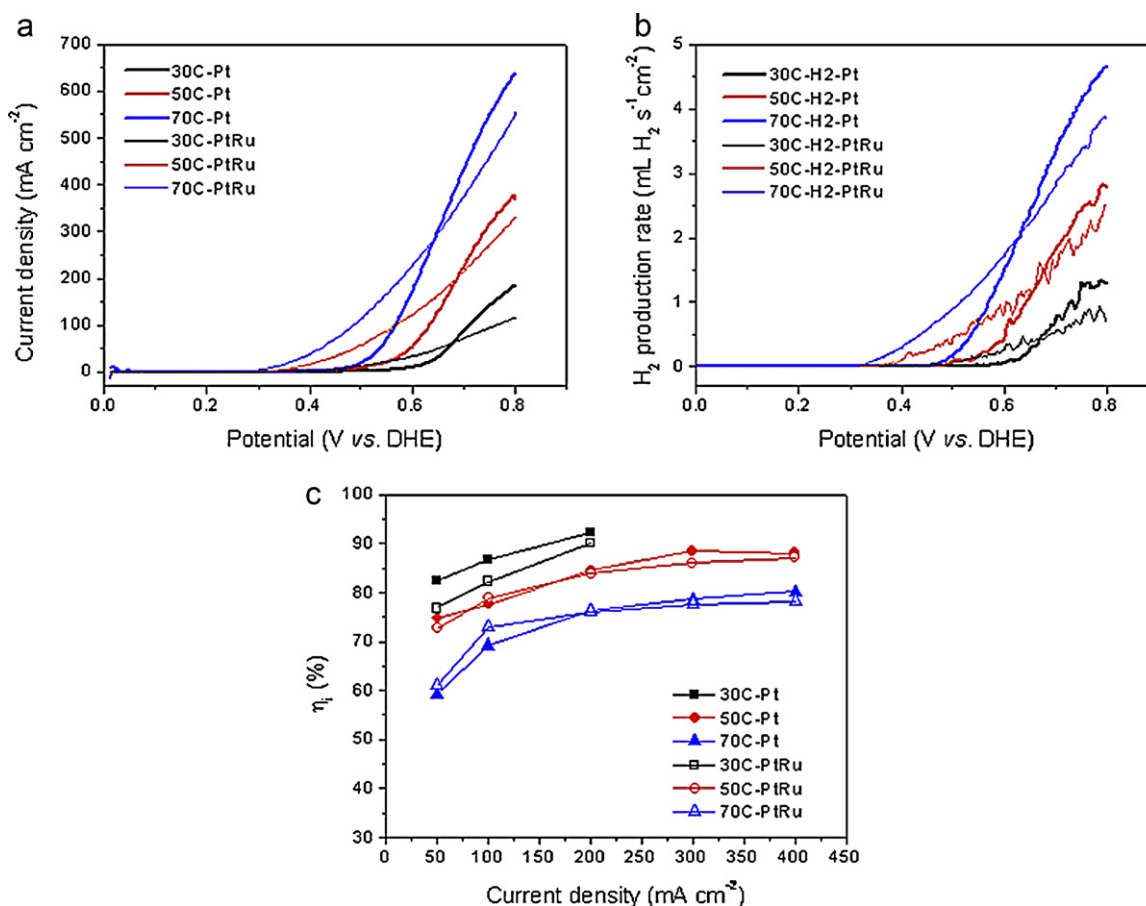


Fig. 4. Comparison of Pt and PtRu on the current variation as a function of applied potential with 1.0M methanol at a scan rate of 5 mV s⁻¹ (a), corresponding hydrogen production rate (b) and current efficiency with respect to cell temperature (c).

react with the oxygenated species present on the neighboring Ru sites in the alloy producing CO₂. Fig. 4 shows the comparison of current variation as a function of applied potential with cell temperature and corresponding current efficiency. As shown in Fig. 4(a) and (b), PtRu catalysts possess lower onset potential for the methanol oxidation over the Pt catalysts regardless of cell temperature. However, Pt catalysts become to outperform PtRu at high overpotential (e.g. >0.63 V at 70 °C) due to higher dehydrogenation capability as well as more enhanced OH adsorbing capability of Pt. Furthermore, judging from the fact that the current efficiency of both catalysts is almost the same over entire current density with the highest value at more than 300 mA cm⁻², Pt could be the more effective electrocatalyst for the methanol electrolysis owing to similar current efficiency and lower overvoltage at high current density. In addition, even though the presence of Ru has been shown to have a dramatic effect on keeping Pt reduced at high potentials in the presence of methanol [15], repeated cycling between oxidizing and reducing conditions or long time operation at high potential, higher than 0.45 V (vs. DHE) could eventually lead to significant ruthenium loss and corresponding loss of catalyst activity [15–19].

Fig. 5 compares the cell voltage and current efficiency variation as a function of time and current density. It is obvious that cell voltage in methanol electrolysis is much smaller than that of water electrolysis by the ca. 1.3 V (see Fig. 5(c)) and more stable at each galvanostatic operation as shown in Fig. 5(a) and (b). The gradual increase of cell voltage at each current density in case of water electrolysis seems to indicate that heat management becomes more critical due to its inherent higher cell voltage. While current efficiency of water electrolysis is almost constant, ca.

83% over the entire current density, methanol electrolysis has 78% current efficiency at 300 mA cm⁻², varying from 60 to 80% for Pt catalysts.

Analyzing the dependence of cell voltage and current efficiency on operating conditions and property of electrocatalysts, we compared the energy requirements necessary to produce the same amount of hydrogen. According to our experiments, on the basis of 300 mA cm⁻² operation with Pt catalysts, the methanol electrolysis can proceed at effective potential of 0.67 V with an energy consumption of ca. 16.2 kWh kg⁻¹ H₂. On the other hand, ca. 46.5 kWh is required to produce 1 kg of hydrogen in our water electrolysis (theoretically 33 kWh kg⁻¹ and typically 50 kWh kg⁻¹ is consumed in a conventional water electrolysis [9]), thereby consuming 65% more energy than a methanol electrolysis. Another featuring point of methanol electrolysis is the purity of hydrogen produced at the cathode side because of the carbon dioxide permeation through polymer membrane that is known to occur in DMFC [7,20–22] as well as direct formic acid fuel cells [23]. From the product analysis by way of gas chromatography, less than 0.8 vol% carbon dioxide was detected in the cathode exhaust. That is much lower amount of carbon dioxide even compared with previous report done by Take et al. [7]. Furthermore, contrary to their results that permeation rates of methanol increases in proportion to the current density, we obtained almost constant or lesser amount of methanol permeated through membrane at the cathode exhaust over the entire current density. Based on some of DMFC researches [21,22], the methanol concentration at the anode catalyst–membrane interface decreases with current density and the methanol crossover decreases as a result. It means that relatively higher current density

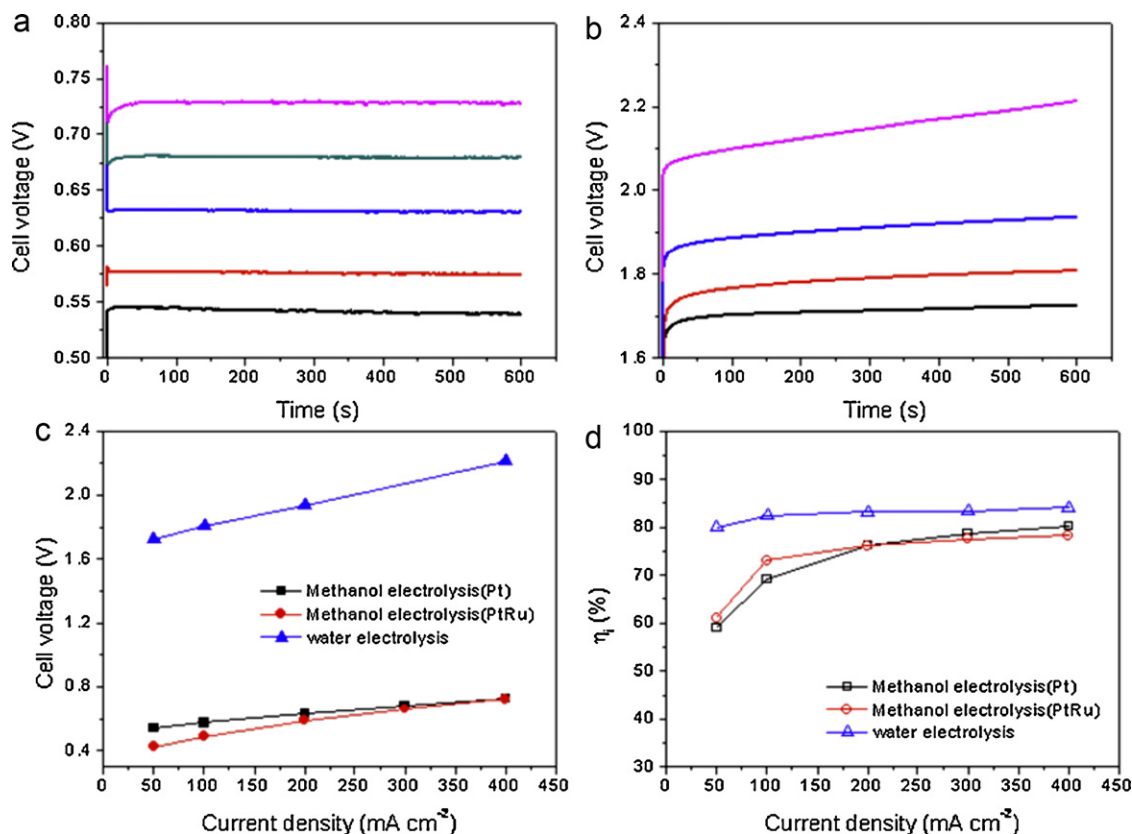


Fig. 5. Comparison of methanol (a) and water (b) electrolysis on the cell voltage variation as a function of time at galvanostatic mode, and cell voltage variation as a function of applied current (c) and corresponding current efficiency (d). All experiments were carried out at 70 °C with 1.0 M methanol.

operation could be more favorable to produce much higher purity hydrogen without methanol residue. In addition, since a membrane in contact with liquid water has a higher water uptake at increasing temperatures [24], and a swollen membrane is more gas-tight, we conclude that the permeation of carbon dioxide in this study is thought to be nearly negligible. An increased swelling of the membrane can lead to a drop in CO₂ diffusion, since it has been observed that only relatively dry or highly hygroscopic conditions, for example 17 M methanol [7,20] or 6 M formic acid [21] in conjunction with CO₂ saturation, may give rise to increase of CO₂ permeation through polymer electrolyte membrane.

4. Conclusions

Operating conditions of the electrolytic hydrogen production by electrochemical reforming of methanol–water solutions are optimized in terms of current efficiency and catalysts stability, and energy requirements were compared with conventional water electrolysis. Current efficiency increases with current density, while decreasing with cell temperature. While PtRu has been known to be best electrocatalyst for methanol oxidation in direct methanol fuel cells, Pt could be the more effective electrocatalyst for methanol electrolysis in terms of current efficiency, cost reduction and stability at high overpotential. Under given conditions, methanol electrolysis can save more than 65% electrical energy necessary to produce 1 kg of hydrogen. For more sophisticated comparison, material cost, especially anode catalysts, and methanol cost should be taken into account, and an alkaline electrolyzer should be considered and compared together.

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