Short communication

Pt-WC/C as a cathode electrocatalyst for hydrogen production by methanol electrolysis

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Abstract

A novel tungsten carbide promoted Pt/C (Pt-WC/C) was prepared by an intermittent microwave heating (IMH) method and used for the cathode electrocatalyst in an electrolyser for hydrogen production by methanol electrolysis. The electrolyser showed better performance for hydrogen production using the Pt-WC/C cathode electrocatalyst than using a commercial Pt/C cathode electrocatalyst. The single cell electrolyser gave reasonable current at voltages lower than 0.4 V. The novelty of this technique is the inherent simplicity and substantially lowered cost.
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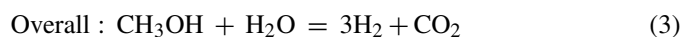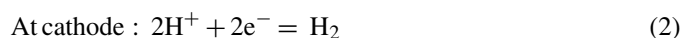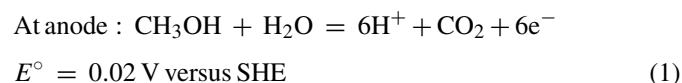
1. Introduction

Hydrogen production by electrolysis of alcohol is simple in principle. As early as 2001, a US patent described hydrogen production by electrolysis of aqueous organic solutions [1]. However, there was no scientific paper in the literature until 2006 [2]. Hydrogen has been considered as an alternative to conventional fossil fuels as an energy source with less environmental damage, greater conversion efficiency and an acceptable cost [3,4]. There are four hydrogen production categories: biological, chemical, electrochemical (water electrolysis; photoelectrochemical; halide electrolysis; H_2S electrolysis) and thermal technologies [5].

Water electrolysis has not had a significant commercial impact because it consumes much electricity which makes the process economically unattractive [6]. It was reported that electrolysis systems based on a proton exchange membrane (PEM) had a number of advantages in comparison with traditional water-alkaline electrolysers, such as ecological cleanliness, a high degree of gas purity and an increased level of safety [7].

The electrolysis system based on a PEM is suitable for portable power applications because it can start up and shut down quickly and can produce hydrogen at a low temperature. Using methanol as the electrolyser feedstock can tremendously reduce the electricity consumption because the standard potential is only 0.02 V versus NHE for methanol oxidation compared to 1.23 V for water, even when the cost of methanol is included, the cost of producing hydrogen by electrolysis of methanol is still only about half that of producing hydrogen by the electrolysis of water [1,2].

The principle of electrolysis of methanol is explained below. Methanol is oxidized via a dehydrogenation process at the anode and the resulting H^+ ions then diffuse through the proton exchange membrane to the cathode chamber where they are reduced to make hydrogen gas [8–10]. Moreover, the hydrogen generated originates not only from the alcohol but also from the water during the electrolysis processes according to the overall Eq. (3):

$$\text{At anode}: CH_3OH + H_2O = 6H^+ + CO_2 + 6e^-$$
$$E^\circ = 0.02\ \text{V versus SHE} \tag{1}$$

$$\text{At cathode}: 2H^+ + 2e^- = H_2 \tag{2}$$

$$\text{Overall}: CH_3OH + H_2O = 3H_2 + CO_2 \tag{3}$$

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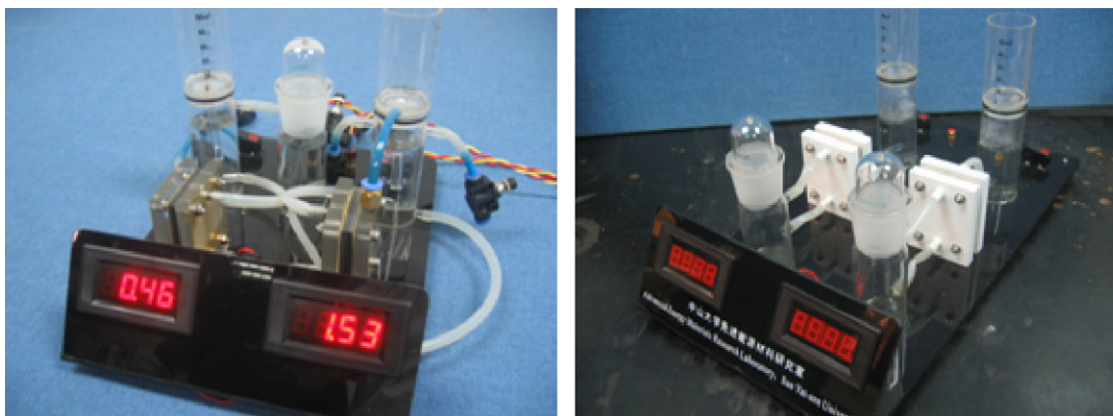 *E-mail address:* stsspk@mail.sysu.edu.cn (P.K. Shen).

Fig. 1. Demonstration kits with the comparison of water electrolysis and methanol electrolysis. The voltages shown in left picture are the voltages for methanol or water electrolysis at the same rate of hydrogen production.

A series of demonstration kits is commercially available as shown in Fig. 1. The US patent claimed that the cathode catalyst is Pt [1]. Pt as a hydrogen evolution electrocatalyst has a high activity and has been widely adopted [2,11–13]. Based on our previous work on oxygen reduction by tungsten carbide promoted Pt/C electrocatalysts (denotes as Pt-WC/C) prepared by intermittent microwave heating (IMH) method [14,15], we report here for the first time the use of Pt-WC/C as the cathode electrocatalyst for hydrogen ion reduction as shown in Eq. (2).

2. Experimental

2.1. Preparation of cathode catalysts

Tungsten powder (1 g) was added to a mixture of 10 mL 30% (v/v) H_2O_2, 5 mL 2-propanol and 10 mL water. The solution was left for 24 h before 1 g of Vulcan XC-72 carbon powder (Cabot Corp., USA) was added. The mixture was treated in an ultrasonic bath to form a uniformly dispersed ink. The ink was dried in an oven and was then heated in a microwave oven (Galanz, WD900ASL23-2, China, 900 W, 2.45 GHz) with a heating procedure of 5 s on and 5 s pause for six times. The dried powder was used as the precursor of the tungsten carbides. The precursor powder in a crucible was bubbled with argon for 10 min and then treated for 10 min continuously by the intermittent microwave heating procedure. Tungsten carbide and 50 wt% Pt/C (Johnson Matthey) were mixed with 2-propanol to prepare composite electrocatalysts. The well-mixed material was treated under ultrasonic stirring for 20 min, for a uniformly dispersed electrocatalyst.

2.2. Membrane electrode assembly (MEA) for electrolyser

The MEA used for the electrolyser was prepared as follows. Carbon paper (TGP-H-060, Toray Industries, Inc., Japan) was used as current collector. The diffusion layer on the carbon paper was composed of 10 wt% PTFE and 1.5 mg cm^{-2} C (Vulcan XC-72R, Cabot Corp., USA). The active surface area of a typical MEA was 2.5 cm × 2.5 cm containing a 2.5 mg cm^{-2} PtRu/C (60 wt%, Johnson Matthey) anode, a 1.5 mg cm^{-2} Pt-WC/C

(WC mixed with 50 wt% Pt/C and Pt:WC = 1:1) or 1.5 mg cm^{-2} Pt/C cathode and a Nafion 117 membrane. The Nafion 117 membrane was successively pretreated in 5 wt% H_2O_2, 1 mol dm^{-3} H_2SO_4 and deionized water for 1 h at 85 °C before use. Lamination was performed by pressing the treated carbon paper onto the membrane at 10 Mpa and 135 °C for 180 s to form the MEA. Fig. 2 shows the schematic diagram of the experimental assembly. The cathode chamber was filled with pure argon prior to the experiment. Methanol aqueous solution was circularly pumped into the anode chamber at a rate of 12 sccm during the electrolysis process. Chemicals were of analytical grade purity and used as received. Methanol solutions with different concentrations were prepared using distilled-deionized water.

2.3. Characterizations

The cathode electrocatalysts were tested in a standard three-electrode electrolytic cell with a platinum foil and a saturated calomel electrode (SCE) as counter electrode and reference
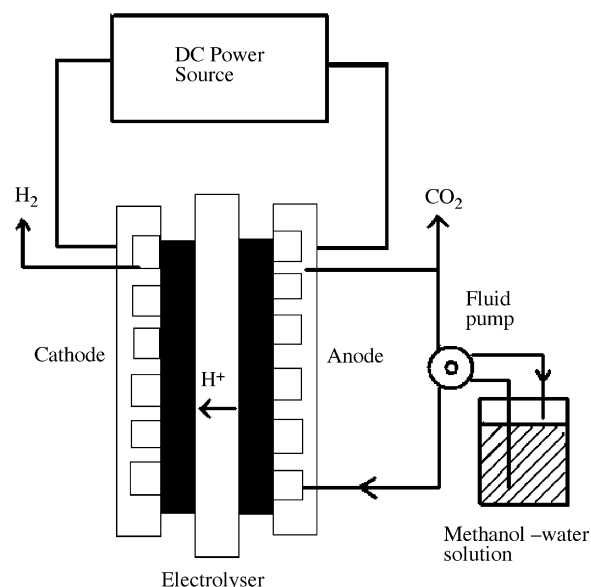

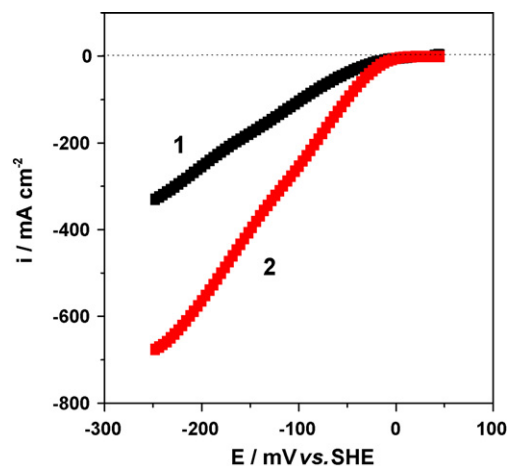Fig. 2. Schematic diagram of the electrolyser.

Fig. 3. Linear potential sweep curves of the HER on Pt/C and Pt-WC/C electrocatalysts in $0.5 \, mol \, dm^{-3}$ H_2SO_4 solution, at the operating temperature of $30 \, ^\circ C$. Scan rate: $10 \, mV \, s^{-1}$. Line 1, 200 µg Pt/C; line 2, 100 µg Pt-100 µg WC/C.

electrode, respectively. Electrochemical measurements were performed on an IM6e Electrochemical workstation (Zahner-Electrik, Germany). A graphite rod with a diameter of 6 mm was used as working electrode substrate and the top surface of the rod was pre-cleaned. Typically, 4 mg electrocatalysts was mixed with 1 mL 2-propanol. The mixture was treated ultrasonically for 20 min for uniform dispersion. A fixed quantity of mixture was then dropped onto the top surface of the graphite rod to produce electrodes with different electrocatalyst loadings. Finally, a drop of 0.5 wt% Nafion suspension (DuPont, USA) was covered on the top to prevent the damage of the electrocatalyst layer.

The performance of the electrolyser was tested on a direct power supply (Yizhan Electronics Co., Ltd., China) under constant current.

3. Results and discussion

Fig. 3 compares the performance of hydrogen evolution reaction (HER) on Pt/C and Pt-WC/C electrocatalysts. The onset potentials for both electrodes are almost the same, however, the addition of tungsten carbide into Pt/C significantly improved the performance for the HER. It is clear that the slope of the current density against the overpotential was sharper for Pt-WC/C than that for Pt/C, showing an increased kinetics.

The performance of MEAs with the cathode electrocatalysts of Pt/C and Pt-WC/C was compared under slow potential sweep and steady-state conditions. Fig. 4a shows the linear potential sweep curves of MEAs with Pt/C and Pt-WC/C cathode electrocatalysts in $2 \, mol \, dm^{-3}$ CH_3OH at very low scan rate of $0.3 \, mV \, s^{-1}$. The MEA with Pt-WC/C cathode electrocatalyst gives the better performance than that of Pt/C cathode electrocatalyst even the Pt loadings in Pt-WC/C cathode electrocatalyst is only a half of that in Pt/C cathode electrocatalyst. The performance of a single cell electrolyser with different cathode electrocatalysts was also tested under steady-state electrolysis. The results are shown in Fig. 4b. As expected that the performance of the electrolyser with Pt-WC/C as cathode elec-
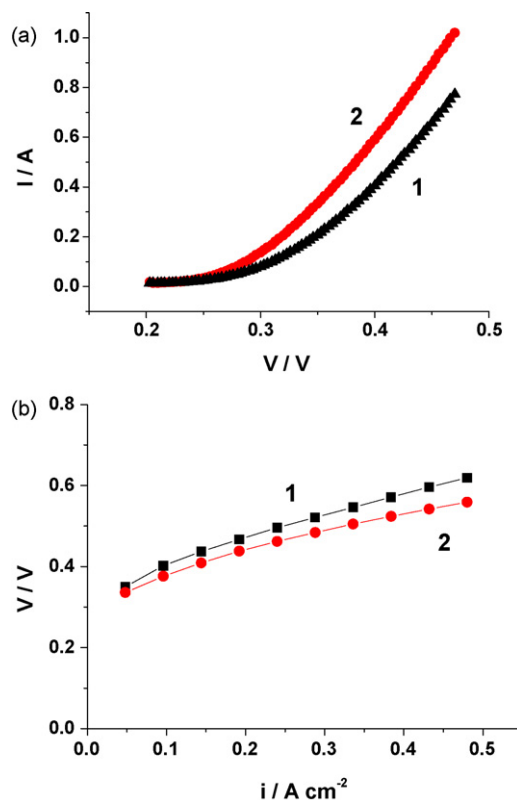

Fig. 4. (a) *E–I* curves of MEAs with (1) Pt/C and (2) Pt-WC/C cathode electrocatalysts in $2 \, mol \, dm^{-3}$ CH_3OH at $90 \, ^\circ C$. Scan rate: $0.3 \, mV \, s^{-1}$. (b) Steady-state *E–I* curves of MEAs with (1) Pt/C and (2) Pt-WC/C cathode electrocatalysts in $2 \, mol \, dm^{-3}$ CH_3OH at $90 \, ^\circ C$. Anode electrocatalyst loadings: $2.5 \, mg \, cm^{-2}$ PtRu/C; cathode electrocatalyst loadings: $1.5 \, mg \, cm^{-2}$ Pt/C or $1.5 \, mg \, cm^{-2}$ Pt-WC/C (Pt:WC/C = 1:1).

trocatalyst is better than that of the electrolyser with Pt/C as cathode electrocatalyst.

The effect of temperature on the performance of the electrolyser was measured in the case of using Pt-WC/C as cathode electrocatalyst. It is obvious that the electrolysis voltage decreases with the increase in temperature. The potential difference could be over 0.2 V at the same current from 30 to $90 \, ^\circ C$ (see Fig. 5). The phenomenon is similar with that of direct methanol fuel cell. The higher temperature is favor to the mass

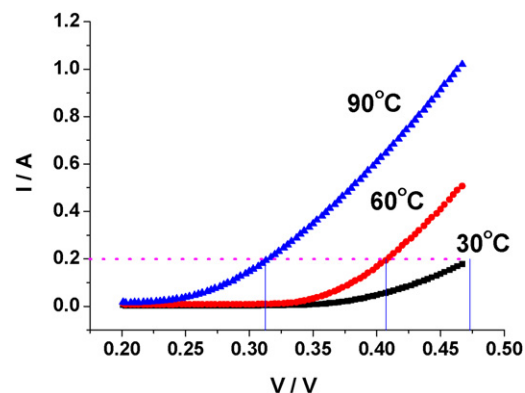Fig. 5. Effect of temperature on the performance of the electrolyser with $1.5 \, mg \, cm^{-2}$ Pt-WC/C cathode electrocatalyst in $2 \, mol \, dm^{-3}$ CH_3OH.
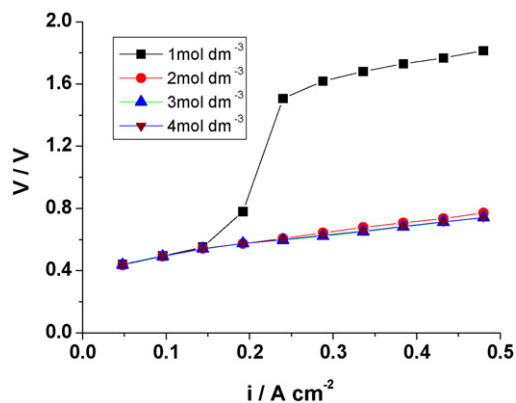
Fig. 6. Steady-state performance of the electrolyser by using different methanol concentrations at 60 °C.

transport and the kinetic processes due to the reduction of the electrochemical and concentration polarizations.

Take et al. used high methanol concentrations up to $17 \, mol \, dm^{-3}$ for hydrogen production by methanol electrolysis [2]. Actually, their results showed that the electrolysis voltage did not depend on the methanol concentration from 3 to $17 \, mol \, dm^{-3}$. We found that the performance of the electrolyser did not depend on the methanol concentration at the methanol concentration higher than $2 \, mol \, dm^{-3}$ operating below 60 °C. However, the concentration polarization is obvious at higher current densities when the methanol concentration was lower than $1 \, mol \, dm^{-3}$ (see Fig. 6). In fact, we found that the performance of the electrolyser became worse at the methanol concentration higher than $5 \, mol \, dm^{-3}$. The season is that even methanol in higher concentrations will not be exhausted at higher current densities, however, the methanol crossover from the anode chamber though the membrane to the cathode chamber produces an undesirable mixed potential at cathode and it reduces the activity of the electrocatalyts. It is clear that the performance of the electrolyser by using Pt-WC/C as cathode electrocatalyst is significant. The single cell voltage for hydrogen production by methanol electrolysis could be lower than 0.4 V at a reasonable current in this study instead of 1 V as reported in literature [2].

The mechanistic study of the HER on Pt-WC/C electrocatalyst is still in progress. A tentative explanation is proposed here and will be justified by the further work. The Pt-WC/C sample was recently analyzed by the X-ray photoelectron spectroscopy (XPS) and found that the surface of the electrocatalyst forms a thin layer of WO_3 in a thickness of several nanometers (data does not show here). The existence of the WO_3 layer would increase the resistance since WO_3 is a semiconductor that will reduce the reaction activity. Tseung's group demonstrated a spill-over effect for the hydrogen evolution on Pt/WO_3 electrocatalyst [16]. WO_3 forms a conducting, blue hydrogen tungsten bronze, H_xWO_3, in acidic media during a hydrogen evolution reaction [17]. In the present case, the nascent H atoms produced by the reduction of H^+ on Pt enters the WO_3 lattice to form hydrogen tungsten bronze, leading to an increase in the conductivity. On the other hand, the rapid removal of the adsorbed H on the surface of Pt would increase the reaction rate.

4. Conclusions

A single cell electrolyser for hydrogen production by methanol electrolysis was fabricated and tested. A tungsten carbide promoted Pt/C (Pt-WC/C) was firstly used as the cathode electrocatalyst to prepare a membrane electrode assembly (MEA) which was finally used in the electrolyser. It was demonstrated that the electrolyser with Pt-WC/C as the cathode electrocatalyst gave a better performance than that of the electrolyser with Pt/C as the cathode electrocatalyst. By using these modified PEMFCs in the electrolysers, any scale requirements can easily be achieved. The combination of this electrolyser concept with solar cells would economically produce hydrogen for storage and subsequent use in, or for in situ use in, fuel cells and chemical engineering applications.

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