

Short communication

Electrochemical characteristics of chloride ion modified Pt cathode in direct methanol fuel cells

Myunghwan Seo^a, Yongsik Yun^a, Jaeyoung Lee^{b,*}, Yongsug Tak^a

^a Department of Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea

^b Fuel Cell Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

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Abstract

We investigated electrochemical characteristics of chloride ion modified Pt (PtCl_m^-) electrode in the electrocatalytic oxidation of methanol, oxidation/reduction behaviours of Pt, adsorption/desorption phenomena of hydrogen. Comparing with pure Pt surface, PtCl_m^- maintained the adsorption activity of proton, hindered oxidation of Pt, induced less binding energy between oxygen and Pt surface. It resulted in the decrease of overpotential of oxygen reduction reaction on the cathodic scan. Thus, PtCl_m^- could increase power performance of direct methanol fuel cell. In addition to activity of PtCl_m^- , the long-term durability of PtCl_m^- cathode was also investigated and it had about five times longer stability.

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1. Introduction

Of late, fuel cells have become a central focus of interest and leading car and power companies are making large-scale investments in fuel cell systems. Fuel cells are set to provide electrical vehicles, small and large scale power stations, and even portable electrical applications such as laptops and mobile phones, with electrical power in a manner which is more efficient and more environmentally friendly than ever before [1–6]. In particular, direct methanol fuel cells (DMFCs) have been considered for use in very small to mid-sized applications due to their high electrical efficiency, long life-time and low poisonous emissions [1–6]. On the other hand, in the operation of DMFCs, there are several problems at a cathode caused by methanol crossover from anode to cathode and it should be solved for the commercialization of DMFC: (i) cathode poisoning by CO adsorption and Pt sintering, (ii) significant fuel loss due to methanol crossover, (iii) decrease partial pressure of oxygen due to water flooding and (iii) temperature dependent power performance. Therefore, cathode catalyst for oxygen reduction reaction (ORR) requires (a) CO tolerance, (b) proton adsorption available, (c) easy oxygen adsorption, (d) ORR kinetics[↑], (e) oxygen storage material, (f) suppression of electro-oxidation of methanol. To our knowl-

edge, no work has been done up to now to study the influence of halide contamination on fuel cell performance. From the data presented previously, Paulus et al. [1] could only point to some aspects which should be considered during MEA production; the degradation of MEA might be occurred due to the dissolution of Nafion by H_2O_2 and it was mainly produced in the reduction of oxygen on a Pt substrate containing chloride ions.

In this work, we tried to develop new cathode catalyst in DMFC via adsorption of chloride ion, which has been known as inhibiting species in most electrochemical studies. The electrochemical characteristics of chloride ion modified Pt cathode in the oxidation of methanol and adsorption/desorption of hydrogen were studied by cyclic voltammetry techniques. The power performance of the single cell and long-term activity of pure Pt and modified Pt cathode was also investigated.

2. Experimental

2.1. Electrode preparation and the modification

A preparation procedure of catalyst ink was well described elsewhere [7] and the catalyst (Pt or PtRu) loading was 3 mg cm^{-2} in each electrode. A geometric active area was 5 cm^2 and catalyst ink was directly spered onto carbon paper. Simple dipping method was used for the chloride ion modification. Pt cathode on carbon paper was dipped in $1 \times 10^{-2} \text{ M KCl}$

* Corresponding author. Tel.: +82 11 9141 1894; fax: +82 2 958 5199.
E-mail address: stmlee@yahoo.com (J. Lee).

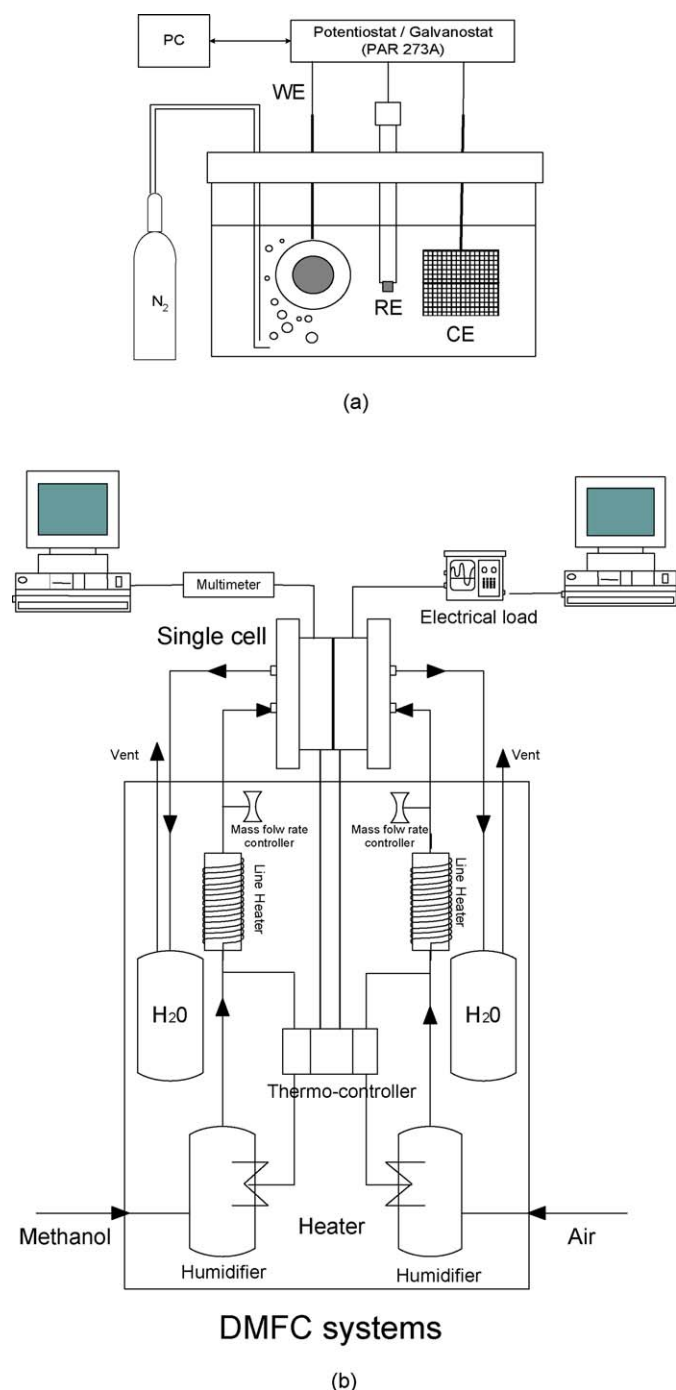


Fig. 1. Schematic diagram of experimental setup for (a) half-cell experiments and (b) single cell measurements.

solution for 5 min and it was rinsed in ultrapure water followed by drying in the oven.

2.2. Half cell measurements

Fig. 1(a) shows the schematic experimental setup for measuring of the electrocatalytic activity of Pt electrode; oxidation/reduction, adsorption/desorption of hydrogen, methanol oxidation. The electrochemical cell body consisted of a glass cylinder capped with a Teflon lid holding all electrodes. The

Pt nanocatalyst sprayed on carbon paper (gas diffusion layer) was used as working electrode (WE). The geometric area of the WE was 0.2 cm^2 . A concentric platinized Pt wire was used as counter electrode (CE). The tip of a Luggin-Haber capillary hosting a SCE reference electrode (RE) was placed in the middle of two electrodes. A potentiostat/galvanostat (EG & G 273A) was used for all cyclic voltammetry (CV) experiments and the data were transferred to an IBM compatible PC controlled by a GPIB interface.

2.3. Single cell experiments

A pair of electrodes (cathode and anode) was hot-pressed on both sides of the polymer electrolyte membrane (Nafion[®] 115, Du Pont) at a temperature of 140°C and with a pressure of 160 kgf cm^{-2} for 240 s. All experiments including electrochemical measurements were conducted with cells, which consisted of MEAs sandwiched between two graphite flow field plates. Current–voltage curves were measured galvanostatically by using an electronic load (EL-200P, Daegil Electronics). In a long-term operation, constant current density of 100 mA cm^{-2} was loaded and galvanostatic current–potential profile. Fig. 1(b) shows the schematic experimental setup for measuring of power performance of the system.

3. Results and discussion

Fig. 2(a) and (b) are cyclic current–potential profile of a pure Pt and chloride ion modified Pt surface (PtCl_m^-) in $0.5 \text{ M H}_2\text{SO}_4$, respectively. Fig. 2(a) shows typical hydrogen adsorption/desorption peak and oxidation/reduction peaks of Pt on the anodic and cathodic scan. On the other hand, we obtain slightly different current–potential profile of modified Pt surface. The desorption/adsorption of chloride ion changes the hydrogen adsorption/desorption reaction and PtCl_m^- suppress the adsorption of oxygen containing species, consistent with previous reports on polycrystalline Pt [7,8]. In addition, the smaller reduction peak occurs at a little bit earlier cathodic overpotential

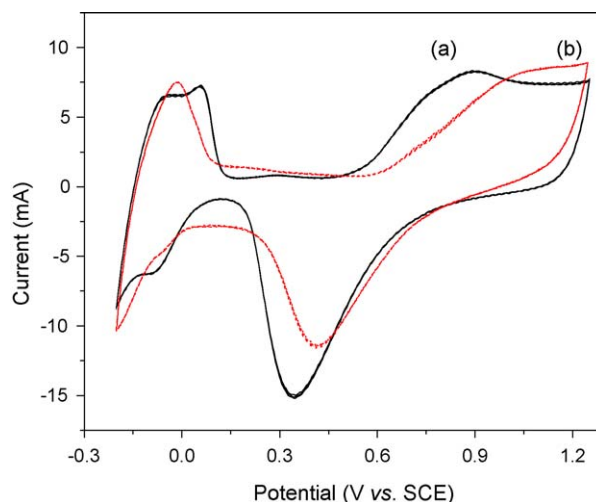


Fig. 2. Cyclic voltammogram of (a) Pt and (b) PtCl_m^- in $0.5 \text{ M H}_2\text{SO}_4$. Scan rate = 50 mV s^{-1} .

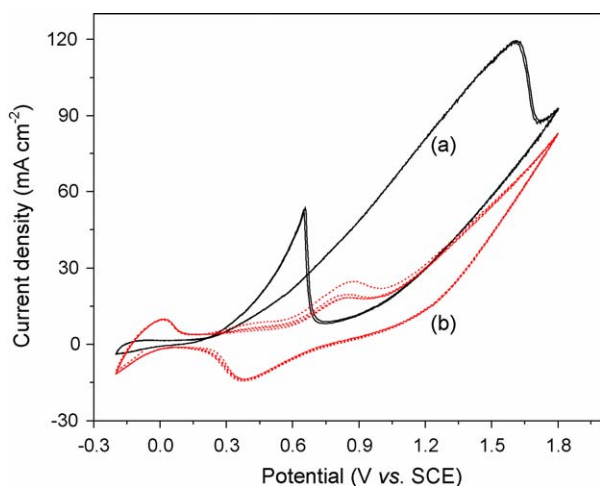


Fig. 3. Cyclic voltammogram of (a) Pt and (b) PtCl_m^- in 1.0 M $\text{CH}_3\text{OH}/0.5$ M H_2SO_4 . Scan rate = 50 mV s^{-1} .

of 0.43 V, which might be attributed the weaker binding energy between Pt surface and oxygen containing species and PtCl_m^- has more doubly layer charge compared with pure Pt surface.

Fig. 3 illustrates the effect of chloride ion modification in the methanol oxidation on Pt electrode. Fig. 3(a) shows the typical CV profile with internal resistance on an unmodified Pt electrode, while no electro-oxidation current of CH_3OH on chloride ion modified electrode is observed (see Fig. 3(b)). In order to oxidize methanol and/or CO on a Pt surface via Langmuir-Hinshelwood mechanism, the adsorption of oxygen containing species is needed. Therefore, the experimental observations in Fig. 3(b) are clearly understood that adsorbed chloride ions inhibits the adsorption of oxygenated species on the anodic scan and it further suppress the oxidation reaction of methanol. The result indicates that in a single cell measurement, crossover methanol could be not oxidized by hindering effect of adsorbed chloride ion on a Pt surface. It could improve the cell performance and induces less fuel loss.

As mentioned in previous study [1], no one tried to study the influence of chloride ions contamination on fuel cell performance. Fig. 4 shows single cell performances with a cath-

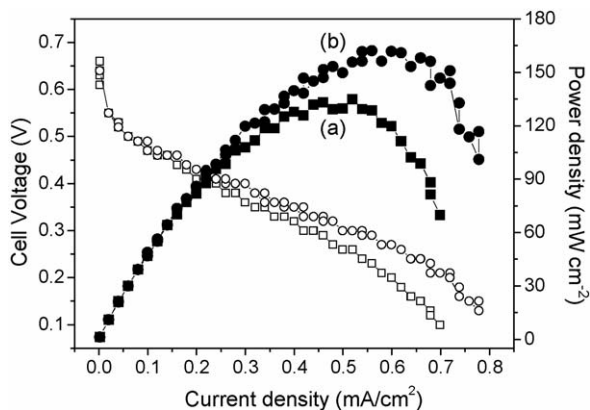


Fig. 4. Single cell current-potential performance of DMFC at 80°C . (a) Without and (b) with cathode modification. Methanol flow rate = $5 \text{ cm}^3 \text{ min}^{-1}$, humidified air flow rate = $1000 \text{ cm}^3 \text{ min}^{-1}$. Electrode area = 5 cm^2 , Ru/Pt (anode) = 3 mg cm^{-2} ; Pt (cathode) = 3 mg cm^{-2} .

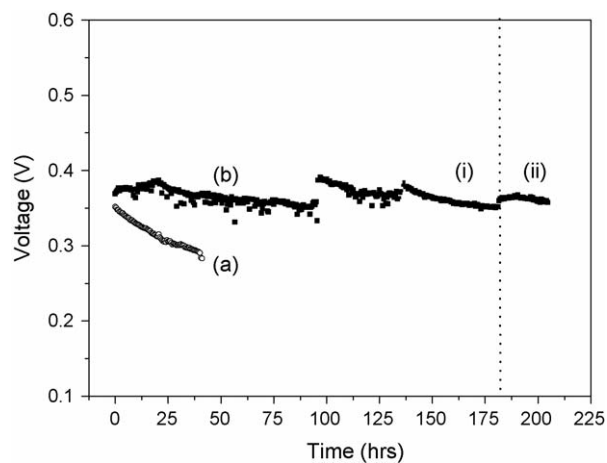


Fig. 5. Cell potential measurement at 100 and 150 mA cm^{-2} . (a) Without and (b) with cathode modification. Electrode area = 5 cm^2 , PtRu (anode) = 3 mg cm^{-2} , Pt (cathode) = 3 mg cm^{-2} . CH_3OH feed = $5 \text{ cm}^3 \text{ min}^{-1}$, humidified air feed rate = $500 \text{ cm}^3 \text{ min}^{-1}$, temperature = 80°C .

ode unmodified and modified by chloride ions. Fig. 4(a) is voltage change and power density with current density when PtRu anode and unmodified Pt cathode are used. The open-circuit-voltage and maximum power density are 0.66 V and ca. 134 mW cm^{-2} , respectively. On the other hand, chloride ion modified Pt (PtCl_m^-) increases the power density of the cell up to 173 mW cm^{-2} , even if OCV is lower than a pure Pt cathode. It is about 30% higher performance than that used a conventional cathode. Its results are due to suppressed electrochemical oxidation rate of crossover methanol on a cathode surface. In other words, the performance of a single cell is strongly dependent of the amount of crossover methanol, i.e. the activity of cathode to oxygen reduction reaction in the presence of methanol on a Pt cathode and inactivity to (electro)chemical oxidation of methanol.

Fig. 5(a) shows the cell voltage of 0.34 V and it continuously decreases until 0.30 V within 2 days and thus, its degradation rate is about 0.83 mV h^{-1} . Fig. 5(b) is the voltage transients at a loading of 100 and 150 mA cm^{-2} , as shown in region (i) and (ii). At a 100 and 150 mA cm^{-2} the cell voltage maintains 0.37 and 0.35 V , representing the power performance between 37 and 53 mW cm^{-2} . Comparing with a long-term stability of the cell used pure Pt cathode, chloride ions modified Pt cathode sustains at least five times longer activity.

4. Conclusions

Methanol crossover is major problem for the commercialization of DMFC, since it leads to a serious decrease in the performance of the cathode, i.e. lower overall fuel cell efficiency. ORR on the cathode in DMFC operation is greatly affected by the ability of Pt to electrochemical oxidation of methanol reached from anode. This problem could be overcome by the development of new cathode that is inactive for methanol oxidation. Modified cathode tolerance to electro-oxidation of methanol was developed by simple dipping method. Both of single-cell activity and long-term stability of PtCl_m^- are better than those from a pure Pt cathode.

Acknowledgements

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