



Influence and mitigation methods of reaction intermediates on cell performance in direct methanol fuel cell system

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ARTICLE INFO

Article history:

Received 8 November 2010

Received in revised form 25 January 2011

Accepted 30 January 2011

Available online 16 February 2011

Keywords:

Direct methanol fuel cell

Gas chromatography–mass spectrometry

Inductively coupled plasma–atomic

emission spectroscopy

Ion exchange resin

Reaction intermediates

ABSTRACT

In direct methanol fuel cells (DMFCs), a dilute methanol and water mixture is generally used and recycled as a fuel to improve the performance and operation time with high fuel efficiency through reduced methanol crossover. Such recycling can, however, allow the continuous accumulation of some reaction intermediates in the circulating loop of dilute methanol during DMFC operation. Therefore, this study examines DMFC contamination sources and the electrochemical influence of recycled methanol fuel by physicochemical analysis of the organic and inorganic (metal) intermediates generated from the DMFC system components. Further, a novel method for mitigating the impact of the reaction intermediates on the performance of DMFC system is proposed.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable attention as clean power source for portable electronic devices owing to their low noise, environmental friendliness and high energy-conversion efficiency. DMFCs also have significant advantages as alternative power sources over direct hydrogen–air fuel cells in terms of storage, start-up, handling and safety issues because they operate under 80 °C and use methanol directly as a fuel [1–3]. Over the last few decades, technological advances in the performance and efficiency of DMFCs have been demonstrated through a range of prototypes, mainly by the world's leading consumer electronics manufactures, such as Samsung, Hitachi and Toshiba [4,5]. Most studies focused on the integration and miniaturization of a DMFC system for portable electronic devices through the development of ancillary balance-of-plants (BOPs) and novel stack designs including high performance and durable membrane electrode assemblies (MEAs) [6–10].

The BOPs for DMFC systems generally consist of heat management (heat-exchangers, fans), power management (con-

trol circuits, batteries) and fuel/water management subsystems (pumps, sensors, gas–liquid separator, fuel/water mixers) [11,12]. In addition, control of the methanol concentration and purity is essential in BOPs because the fuel efficiency and power density decrease if the methanol concentration is too high due to the mixed potential and carbon dioxide formation at the cathode side caused by increased methanol crossover [13,14]. During DMFC operation, dilute methanol at a specified concentration enters the anode of the stack. The concentration of the methanol solution exiting the stack is reduced by the water produced by the electrochemical reactions at the cathode in the mixing tank (sometimes called the recycler). Pure methanol then needs to be added from a fuel cartridge to recover the solution to the original concentration. Some intermediates and by-products are possibly produced in the electrochemical reactions during DMFC operation [15,16]. Contaminants that originate from stack component materials can cause serious performance degradation [17–19]. In addition, Na⁺ and Cl⁻ are likely impurities in water contained in the humidified gas and methanol solution, as well as in the atmosphere as an aerosol in coastal areas and a deicer on roads during winter [20,21]. Furthermore, Pt-based catalysts are usually synthesized from chloride-containing precursors. The cell performance can be affected by these materials, which sometimes causes permanent damage to the DMFC stack [21–24]. Moreover, these products accumulate continuously in the circulating loop of dilute methanol with time. In addition, some metal ions can be produced from the

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corrosion of heat-exchangers, stack or other system components [25,26].

Information on the effects of the organic and inorganic (metal) contamination generated from a DMFC system BOP is limited. Furthermore, no studies have provided mitigation strategies for the electro/physicochemical poisoning effect of the recycled methanol fuel on the DMFC stack. This study examines the electrochemical effect of recycled methanol fuel through physicochemical analysis of the reaction intermediates and by-products generated from the DMFC system components. In addition, an effective control strategy for minimizing the impact or recovering the performance of a DMFC system is proposed.

2. Experimental

2.1. Preparation of stack (MEAs)

The membrane electrode assemblies (MEAs) were prepared from a hydrocarbon-based membrane (a sulfonated polyethersulfone-based ionomer) with Pt/Ru black (Hispec 6000, Johnson Matthey) and Pt black (Hispec 1000, Johnson Matthey) as the anode and cathode catalysts, respectively. The catalyst loading for both electrodes was 6 mg cm^{-2} and the active area of the MEAs was 14 cm^2 . SGL carbon paper (25BC brand, Germany) was used as the gas-diffusion layer (GDL) for each electrode. The MEAs were fabricated by hot pressing the catalyst-coated GDLs on to a membrane.

The DMFC stack was composed of 24 MEAs, rectangular graphite blocks with serpentine flow-fields (Ildo, Korea), and a pair of gold-plated stainless-steel sheets as current-collectors. Ethylene propylene diene monomer (EPDM) rubber gaskets (Dong-A Hwa Sung Co., Korea) were used to prevent methanol and air leakage inside the stack owing to their high water, thermal and chemical resistance. A stack consisting of the MEAs, bipolar plates, current-collectors and end plates was clamped with four bolts. The bolts through the two end-plates were fastened down with a torque wrench so that an even pressure was applied over the entire surface of the end-plates. The compression ratio of the MEA in the stack was adjusted to 15% with gaskets, which varied in thickness, compared with the initial thickness of the stack.

2.2. Preparation of DMFC system

A schematic diagram of the DMFC system test set-up consisting of the stack, fuel mixer, fuel cartridge, pumps and heat-exchangers

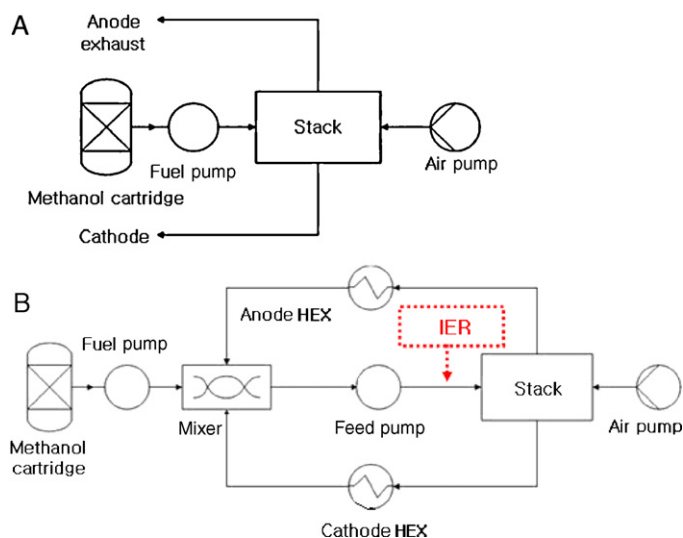


Fig. 1. Test set-up of (a) open-loop and (b) close-loop DMFC system.

(HEX) is given in Fig. 1. The open-loop DMFC system (Fig. 1a) allowed a fresh 1 M methanol solution to be supplied continuously to the stack by a pump (Ismatec, Switzerland) without recycling the reacted fuel and water produced. In contrast, pure methanol (99.9%, Samjung, Korea) was pumped into the mixing chamber to maintain a constant methanol concentration in the closed-loop system (fuel pump: IDEX Health and Science, USA, feed pump: KNF, Germany), as shown in Fig. 1b. In the mixing tank, the methanol reacted from the anode was also mixed with water produced from the electrochemical reactions at the cathode. A 1 M methanol solution controlled automatically within a 0.2% error by a methanol sensor (Sensirion, Switzerland) was supplied to the stack anode as a fuel. In the closed-loop system, the HEXs made from SUS 304 were installed at the stack outlet to control the amount of liquid and vapor properly through the reduced temperatures of the reacted fuel and air. To remove or minimize the impurity effect on DMFC performance, ion-exchange resins (IERS, Amberject UP6150, UP1400, U4000, Rohm and Haas) were introduced to the DMFC system between the methanol feed pump and inlet of the stack anode, as shown in Fig. 1b, and the electrochemical results were compared with the case without an IER.

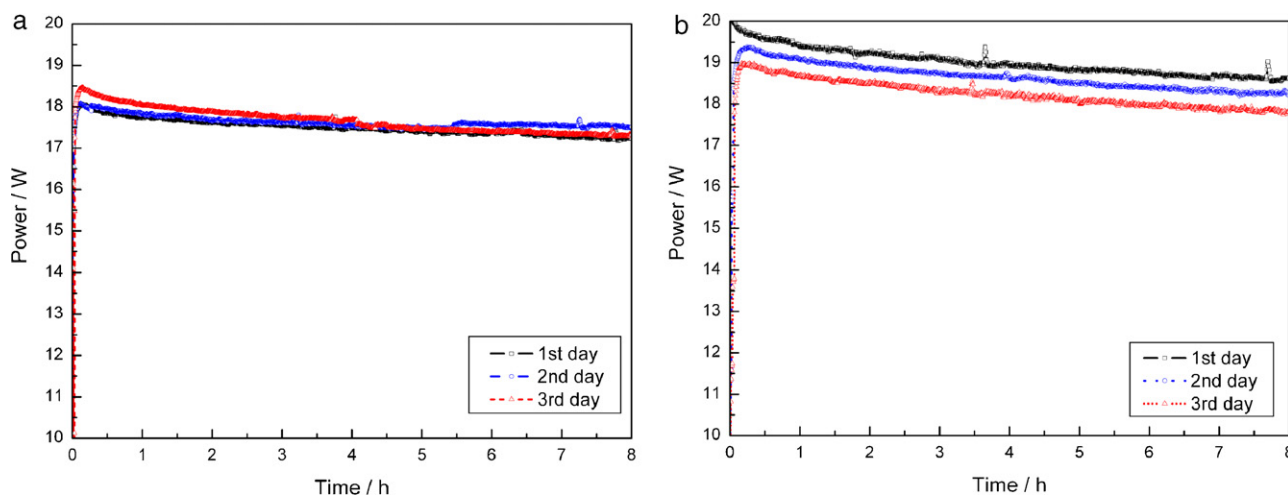


Fig. 2. Performance of stack in response to electronic load (123 mA cm^{-2}) in (a) open-loop and (b) close-loop DMFC system.

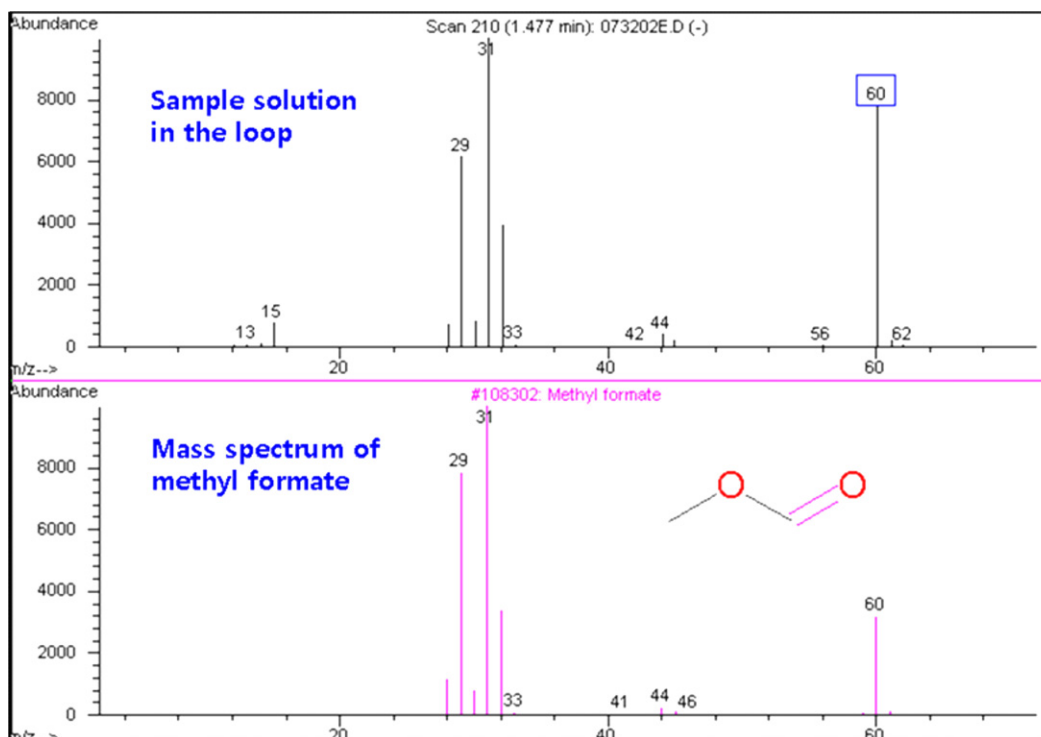


Fig. 3. Chromatographic separation of recycled methanol fuel, extracted from mixer after 16 h operations of DMFC.

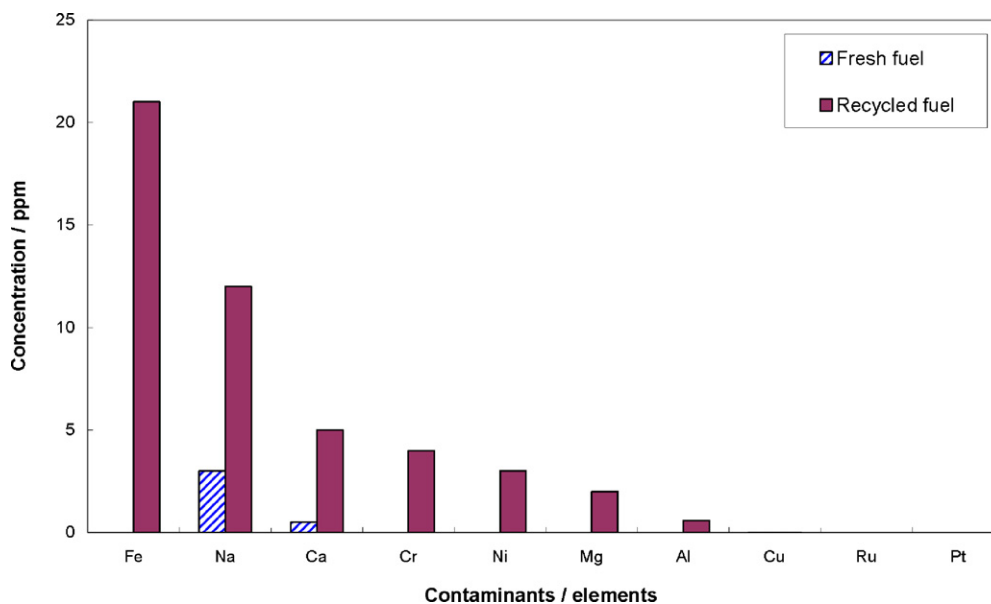


Fig. 4. ICP-AES analysis of recycled methanol fuel.

2.3. Electrochemical tests and physicochemical analysis of DMFC system

All electrochemical tests of the DMFC were controlled by means of a test station (Arbin Instruments, USA). A thermocouple was embedded in the end-plate to monitor the operating temperature. The DMFC performance was evaluated by current–voltage polarization and constant-current testing (123 mA cm^{-2}). The flow was set to a stoichiometry of 2.5 of 1 M MeOH and dry air. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer, Optima-4300DV, USA) and gas chromatography–mass spectrometry (GC–MS, JEOL JMS-600W, Agilent 6890, Japan) were carried

out for physicochemical analysis of the recycled methanol fuel and stack MEAs in the DMFC system. Field-emission-scanning electron microscopy and energy-dispersive X-ray spectroscopy (FE-SEM/EDS, JEOL, Japan) were also used to examine closely the degradation phenomena of the DMFC system during DMFC operation.

3. Results and discussion

3.1. Electrochemical performance tests of DMFC system

The electrochemical performance of the open-loop DMFC system (Fig. 1a) was tested without recycling the reacted fuel and

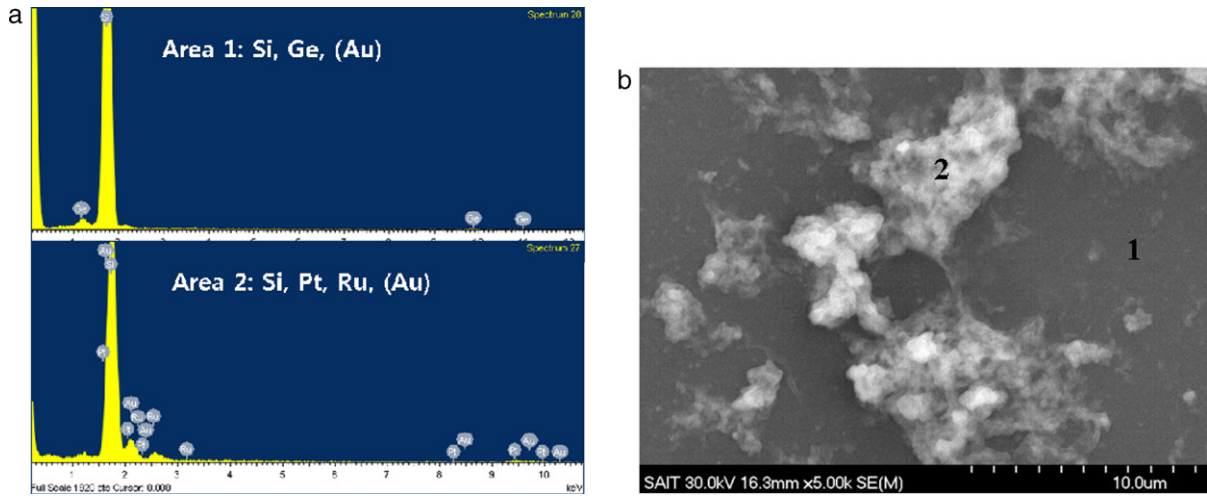


Fig. 5. Post-mortem (a) EDX analysis and (b) SEM image of methanol sensor.

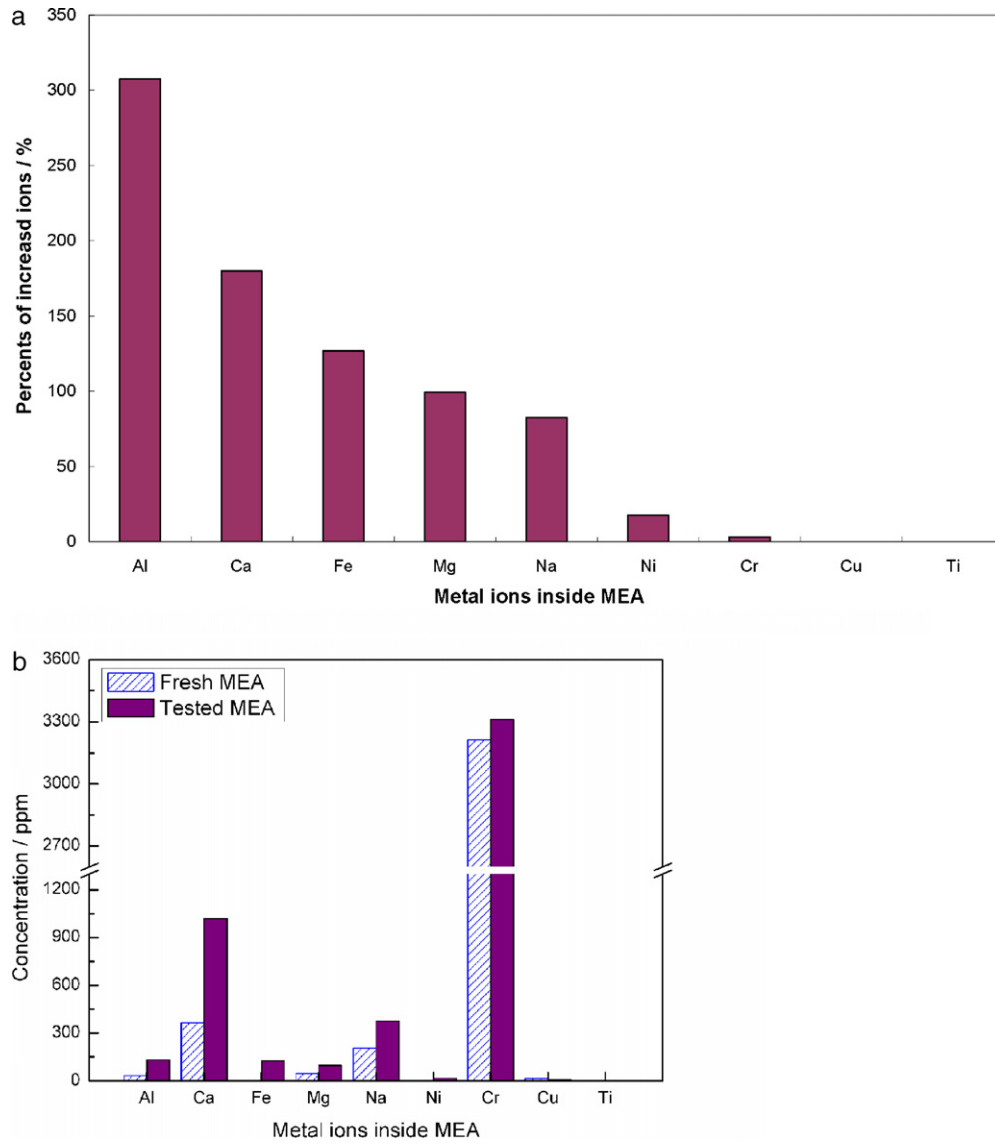


Fig. 6. (a) percentage concentration and (b) absolute concentrations of increased ions inside the MEA by ICP-AES analysis before and after constant-current testing in closed-loop system.

water produced. Fig. 2a shows the performance of the stack in response to the electronic load (123 mA cm^{-2}), maintaining a supply of 1 M methanol and air with a stoichiometry of 2.5 at approximately 65°C . The DMFC produces stable power in constant-current operation without degradation of the daily investigation for several days. On the other hand, with a closed-loop control DMFC system (Fig. 1b), the performance of the stack decreased gradually each day, as shown in Fig. 2b.

The performance degradation, which occurred within several days, might be due to the gradual build-up of organic and inorganic contaminants generated by a range of electrochemical reactions at both the cathode and the anode sides. This is because the methanol solution as a fuel was recycled continuously in a closed-loop system, which included the stack and HEXs, during DMFC operation. Therefore, the cell resistance could be increased via augmentation of the reaction intermediates and by-products in the fuel loop because these contaminants prevented proton conduction in the membrane and electrochemical reactions in the electrode, resulting in decreased cell performance. To confirm this, the recycled fuel was analyzed physicochemically after electrochemical tests of the system; the results are discussed in the next section.

3.2. Physicochemical analysis of recycled methanol fuel

The reaction intermediates travelling the closed-loop system during DMFC operation were first analyzed by GC-MS. Organic intermediate oxidation products can poison the electrocatalyst surface by adsorbing strongly and obstructing further oxidation. The chromatographic separation of the recycled methanol fuel, which was extracted from the mixer after 16 h of constant-current operation, is presented in Fig. 3. The dominant chromatograms at 29, 30, 33 and 60 correspond to the features of methyl formate. Other fragments originate from the methyl group of the methanol solution. On the other hand, formaldehyde and formic acid cannot be differentiated easily from the methanol chromatograms, even though they are well-known by-products of the methanol oxidation reaction. This may be because these species actually form during DMFC operation but are consumed readily due to their facile oxidation on Pt-Ru catalysts [15]. Moreover, methyl formate and formic acid are oxidized anodically using a Pt and Ru electrocatalyst at the DMFC operating temperature and potential. The rate of the methyl formate reaction is faster than that of the anodic oxidation of methanol, and is dependent on potential and temperature [2–4]. Therefore, methyl formate may not exert an adverse effect on cell performance within short-term DMFC operation. Further studies of the long-term durability of

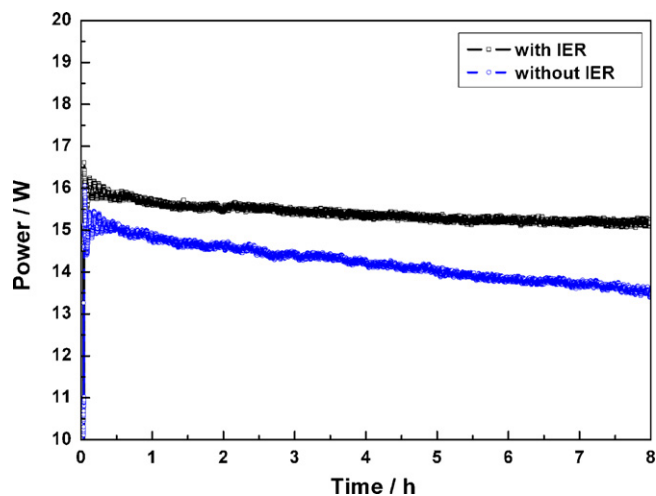


Fig. 7. DMFC stack performance with and without IER in constant-current operation mode.

the DMFC system exposed to methyl formate and formic acid are required.

The ICP-AES results of the recycled fuel after 16 h of constant-current operation are given in Fig. 4. According to ICP-AES, the recycled fuel contain some heavy metal cations, such as Al^{3+} , Mg^{2+} , Ni^{2+} , Ca^{2+} , Na^+ , Fe^{2+} and Cr^{3+} . Large quantities of Pt and Ru are also discovered in the methanol sensor through post-mortem EDX analysis of the system, as shown in Fig. 5a, even though they are not detected in the recycled fuel by ICP-AES. Fig. 5b shows SEM images of the inner surface of the methanol sensor. Zone 2 is the sensor surface contaminated by Pt and Ru, whereas zone 1 is the pristine sensor surface. Pt has been reported to be susceptible to leaching out from the highly active Pt-Ru catalyst, even under normal DMFC operating conditions, because the anode is exposed continuously to a high potential by the operating voltage for the long-term testing [28].

To investigate the degradation mechanisms of the DMFC in more detail, ICP-AES was used to examine the MEA before and after the constant-current testing in the closed-loop system for 16 h. As shown in Fig. 6a, the concentrations of metal ions inside the membrane increase significantly after electrochemical tests in the closed-loop. In particular, the concentrations of Al^{3+} , Ca^{2+} , Fe^{2+} , Mg^{2+} and Ni^{2+} increased by 307%, 179%, 127%, 99% and 18%, respectively, after the recycling tests. The absolute concentrations of metal ions inside the MEA before and after testing in the closed-loop system are shown in Fig. 6(b). This suggests that the stainless-

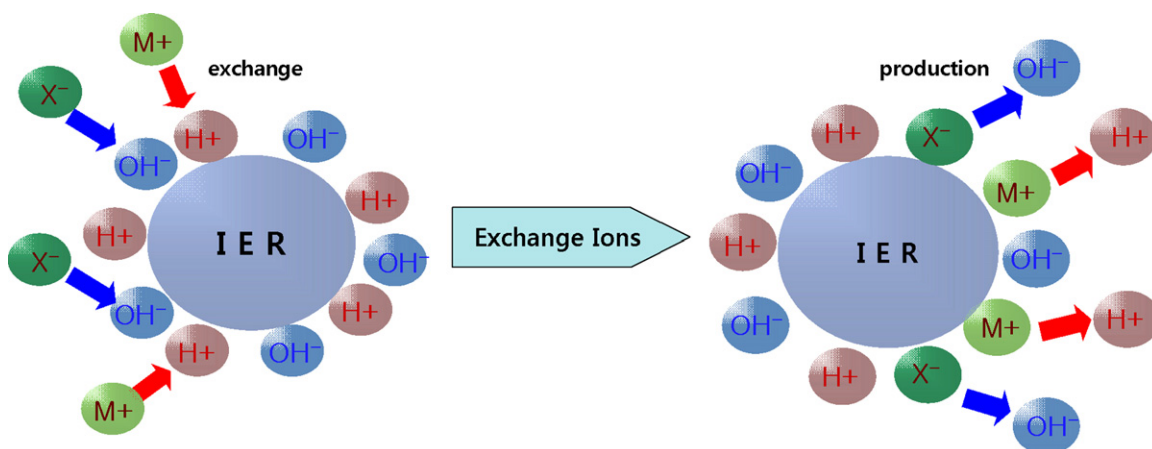


Fig. 8. Schematic diagram of mechanism of ion-exchange phenomena in the IER.

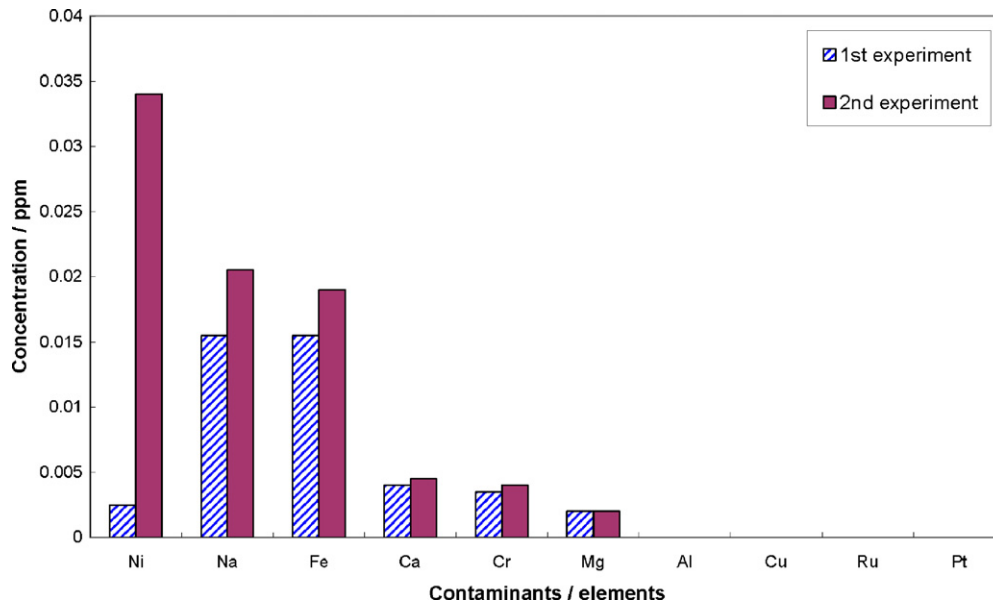


Fig. 9. Concentrations of trapped metal ions by an inspection of IER after DMFC operation.

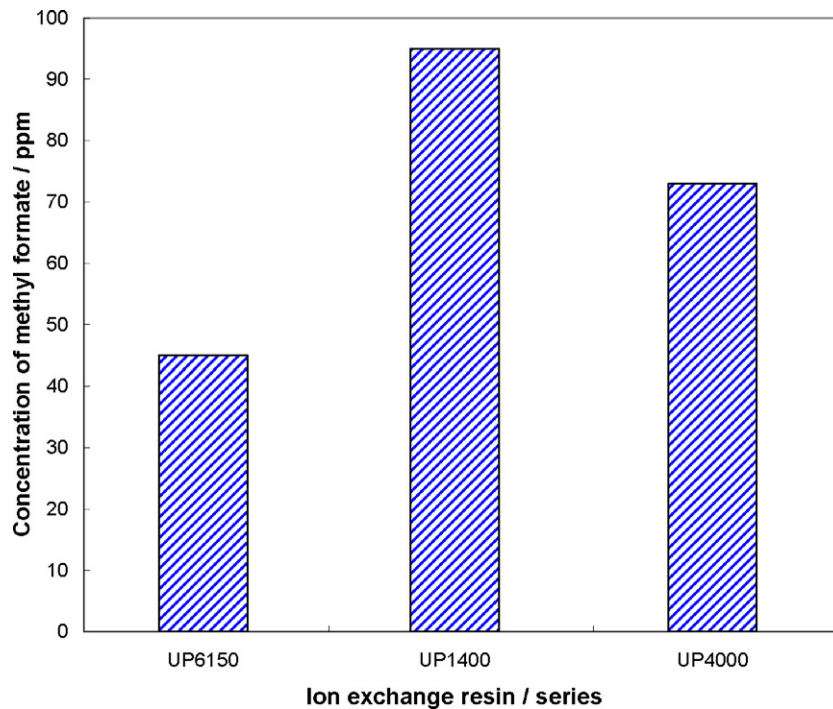


Fig. 10. Concentration of methyl formate trapped by IER after DMFC operation.

steel constituents, such as Al, Cr, Fe and Ni, which leach from the stack components and heat-exchangers are the main source of contamination in the recycled fuel. In particular, the cations decrease the proton conductivity by occupying the conducting sites with a lower water content [23,25]. These also have an adverse effect on the catalytic oxidation of methanol on the surface of the Pt electrode [26]. Metal ions inside a MEA might accelerate membrane failure through peroxide formation [23,24,27]. In addition, Pt and Ru decompose from the MEA electrodes and are detected by the methanol sensor as one of the impurities in the fuel and accumulate continuously in the circulating loop of dilute methanol with time. This results in a dysfunction of the methanol sensor and methanol pump during the long-term durability tests of the DMFC

system. These contaminants which are introduced into the cell via the feed-stream, have an adverse effect on the performance of the DMFC MEAs. Ca^{2+} and Na^{+} ions, however, do not affect the performance degradation of the DMFC in additional testing (data not shown) despite being detected at relatively high concentrations by ICP-MS. Ca^{2+} and Na^{+} ions are believed to have entered the DMFC system from body sweat or latex-gloves during MEA fabrication or physicochemical analysis.

3.3. Mitigation strategy against recycled methanol fuel

Ion-exchange resin (IER) was introduced to the DMFC system to remove or minimize the impurity effect on the DMFC performance.

IER can easily release and trap specific ions due to the developed pore structures on the surface, and is commonly used for water purification and metal separation [29–32]. Therefore, in this study, a combination of cation and anion exchange resin was installed in the inlet of the stack anode, as shown in Fig. 1b. The stack performance in the closed-loop DMFC system with and without IER is given in Fig. 7. Interestingly, the degradation of the stack by fuel contaminants is mitigated by the IER in constant-current operation mode (123 mA cm^{-2}) for 8 h. On the other hand, the stack performance decreases remarkably (8.8%) without a IER. This may be due to the removal of contaminants in the recycled fuel by the IER. In other words, the IER takes up all metal cations and anions, and release H^+ and OH^- , respectively, to produce a pure methanol fuel. The H^+ and OH^- then react together to produce more fresh water. The mechanism of the ion-exchange phenomena in the IER is shown in Fig. 8.

This was confirmed by ICP-AES analysis of the reacted methanol solution and the used IER, as shown in Fig. 9. The same experiment (#1 and #2) was performed twice to confirm the results and examine the concentration of contaminants according to the testing time. ICP-AES of the recycled fuel after DMFC operation for approximately 16 h with the IER shows that the concentrations of contaminants are below the detection limit. On the other hand, post-mortem analysis of the IER after constant-current operation reveals an increase in the concentration of metal ions. Furthermore, the concentrations of contaminants increase with increasing testing time (frequency). This occurs because IER traps metal ions in the reacted methanol solution, releasing H^+ and OH^- on the developed pore structure, as shown in Fig. 8. In addition, the IER traps methyl formate and various metal ions in the recycled fuel, as shown in Fig. 10.

As another mitigation strategy, the degraded DMFC stack by the metal ions was purged by flowing deionized water through the anode for 15 min to remove reaction intermediates. Nevertheless, complete recovery of the DMFC stack performance is not achieved, even after purging the stack anode with deionized water. This may be due to the contaminants imbedded in the membrane and Pt electrocatalysts, which have not been removed completely by water. Therefore, the reaction intermediates cause permanent performance loss through MEA degradation.

4. Conclusions

A DMFC stack undergoes a gradually decrease in performance with increasing operation time due to a gradual build-up of intermediates and contaminants that are generated by electrochemical reactions in the system. ICP-MS and GC-MS confirm this phenomenon by the quantitative detection of a number of methanol reaction intermediates moving through the fuel loop of the system. A DMFC system composed of an IER, which is located in the inlet of the stack anode, is designed as a mitigation strategy. The DMFC system with a IER takes up all contaminants and releases H^+ and OH^- to provide fresher fuel, thereby mitigating stack degradation by fuel contaminants. Nevertheless, further studies of the degree and lifetime of the ion exchange effect from the different cations and anions in the IER are required.

Acknowledgements

This study was supported by the Energy & Materials Research Lab of Samsung Advanced Institute of Technology (SAIT), Samsung Electronics and the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy (#10037289, “Development of Highly Active and Sustainable Hybrid Catalysts”).

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