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Highly durable direct hydrazine hydrate anion exchange membrane fuel cell

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HIGHLIGHTS

- Degradation factors of DHFCs were analyzed by in-situ soft X-ray radiography.
- Durability of DHFCs was significantly improved by MSR technology.
- PEM was integrated into AEM of DHFCs.

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ABSTRACT

The factors influenced on degradation of direct hydrazine hydrate fuel cells (DHFCs) under operation conditions are analyzed by in situ soft X-ray radiography. A durability of DHFCs is significantly improved by multi-step reaction DHFCs (MSR-DHFCs) approach designed to decrease the crossover of liquid fuel. An open circuit voltage (OCV) as well as cell voltage at 5 mA cm⁻² of MSR-DHFC construct with commercial anion exchange membrane (AEM) maintained for over of 3500 h at 60 °C. Furthermore, the commercial proton exchange membrane (PEM) is integrated into AEM of MSR-DHFCs resulting in stable power output of MSR-DHFCs for over than 2800 h at 80 °C.

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1. Introduction

Among of several renewable energy sources fuel cell (FC) technology is fastest growing and can be considered as most promising for market penetration in different consumers' areas, from mobile to automobile applications. The possibility of using the different fuels places fuel cells on the top of environmentally friendly energy conversion approaches [1–8]. The intrinsic thermodynamic properties of different chemical compounds which can be used as fuels

in FCs are listed in Table 1. The hydrazine hydrate (HH) attracts the attention of researchers as a potential fuel due to the combination of high energy density, ease of logistics (liquid fuel) and absence of carbon atoms in its molecule. Last one is extremely important for creation of technology with zero carbon dioxide emission. This fuel is already used in direct hydrazine hydrate fuel cell vehicles (DHFCVs) which have a unique feature of complete absence of platinum group metals (PGMs) in both: anode and cathode side of membrane electrode assembly (MEA) as well as utilization of anion exchange membrane (AEM) separators and ionomers [9–13]. The carcinogenic risk of hydrazine hydrate, class 2B by International Agency for Research on Cancer (IARC) report, is equivalent to one of

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Table 1
Thermodynamic data of fuels ($-\Delta H$: Enthalpy, $-\Delta G$: Gibbs free energy, ϵ : theoretical energy conversion efficiency, E^0 : cell voltage, $E.D.$: energy density).

Fuel	Reaction	$-\Delta H$ [kJmol ⁻¹]	$-\Delta G$ [kJmol ⁻¹]	ϵ [%]	E^0 [V]	$E.D.$ [kWhL ⁻¹]	Remarks
Methanol	$\text{CH}_3\text{OH}_{(l)} + (3/2)\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}_{(l)}$	726	702	96.7	1.21	4.82	25 °C/1 atm
Ethanol	$\text{C}_2\text{H}_5\text{OH}_{(l)} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}_{(l)}$	1367	1325	96.9	1.15	6.28	25 °C/1 atm
Borohydride	$\text{BH}_3(\text{aq}) + 2\text{O}_2 \rightarrow \text{BO}_2(\text{aq}) + 2\text{H}_2\text{O}_{(l)}$	357.8	325.6	91.0	1.64	7.31	25 °C/1 atm
Formic acid	$\text{HCOOH}_{(l)} + (1/2)\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}_{(l)}$	254.3	270	106.2	1.40	1.75	25 °C/1 atm 88 wt%
2-Propanol	$\text{C}_3\text{H}_7\text{OH}_{(l)} + (9/2)\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}_{(l)}$	2005.6	1948	97.1	1.12	7.08	25 °C/1 atm
Dimethyl ether	$(\text{CH}_3)_2\text{O}_{(g)} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}_{(l)}$	1460.3	1387.2	95.0	1.20	5.61	25 °C/1 atm
Ammonia	$\text{NH}_3(\text{g}) + (3/4)\text{O}_2(\text{g}) \rightarrow (3/2)\text{H}_2\text{O}_{(l)} + (1/2)\text{N}_2(\text{g})$	383	339	89	1.17	3.3	25 °C/11 atm
Hydrogen	$\text{H}_2(\text{g}) + (1/2)\text{O}_2 \rightarrow \text{H}_2\text{O}_{(l)}$	285.8	237.1	83.0	1.23	0.18	25 °C/68 atm
Hydrazine	$\text{N}_2\text{H}_4(\text{l}) + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}_{(l)}$	622.2	623.4	100.2	1.61	5.40	25 °C/1 atm
Hydrazine hydrate	$\text{N}_2\text{H}_4(\text{l}) + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}_{(l)}$	606	602	99	1.56	3.24	25 °C/1 atm

gasoline so careful handling of the fuel is required with the safety regulation approved for gasoline industry. It also should be mentioned that relative carcinogenic influence of hydrazine found in carcinogenicity studies clear shown that there is no increase of cancer cases for workers in a hydrazine production plants [14,15]. The combination of mentioned above factors allows to build the inexpensive AEMFCs systems and decrease the influence of volatile PGM market on this technology. It should be mentioned, that investment of funding and man power in the AEMFC R&D resulted in substantial increase in performance of this type of fuel cells [16–18]. Having breakthrough in activity the durability of alkaline exchange fuel cells is still an issue, which should be addressed This issue was summarized and discussed by Dekel et al. recently [19]. Among the several degradation factors crossover of liquid fuel from anode to the cathode of MEA is critical technical issue and performed durability tests reported in literature estimated the AEMFCs life-time on the range of 100–800 hrs [19].

In this study, we focus on the increase of durability of DHFCs by designing the improved anode catalyst layer. The degradation factors in operating DHFCs were analyzed by in-situ soft X-ray radiography. It was found that durability of DHFCs can be significantly improved by multi step reaction DHFCs (MSR-DHFCs) technology in order to decrease the crossover of liquid fuel. The original OEM durability testing protocol was developed and important electrochemical parameters of MEA such as: open circuit voltage (OCV), cell voltage, power density, and potential of both electrodes were evaluated. Commercial AEM and proton exchange membrane (PEM) were integrated into AEM of MSR-DHFCs resulting in stable power output of MSR-DHFCs for over of 2500 h (AEM) and 1600 h (PEM), which is state-of-the-art value for first time published in open literature.

2. Experimental

2.1. Soft X-ray radiography

The visualization was performed by using a laboratory-base soft X-ray radiography (Mars Tohken Solution Co. Ltd. TUX-9000D) setup. The system was developed by Hirai and Tsushima group [20–27] in order to have high spatial and time resolution. The schematics and photo representation of soft X-ray radiography setup is shown on Fig. 1. A tungsten thin-film was used as the target material for generating soft X-rays ($W_{L\alpha}$; 8.40 keV, $W_{L\beta}$; 9.67 keV), and the X-ray tube voltage was set at 30 kV. Alignment was performed before observing the fuel cell by using a micro-chart (JIMA RT RC-02), by which a line pitch of 1.0 μm could be discriminated at the cell position. The cell was carefully fixed on a computer controlled four-axis stage that was able to move in the X, Y, and Z directions with a resolution of 1 mm and rotate around the Z axis. The stage allowed accurate alignment of the cell with the X-ray

beam. The cell plane was adjusted to be perpendicular to the X-ray beam. The center of the membrane was aligned with the center of the image detection area of through-plane cell, which was along the beam axis. The images were captured by an imaging system comprised of 1024 \times 1024 pixel electron multiplication charge-couple device (EM-CCD) camera (Princeton Instrument, PIXIS-XB-1024BR) and processing computer. All the images were taken at 1.6 frame per second (fps), and an image with 2 s of integration time was used to calculate the gas distribution. Image-J (National institute of health) software was used for image processing.

2.2. Visualization cell

In order to observe a media mass-transfer inside of the cell by soft X-ray radiography and prevent the liquid fuel leakage during the observation, the through-plane direction cell was designed and fabricated (Fig. 2). The soft X-ray transparent carbon current collector with the active areas of the through-plane cells of 0.35 \times 0.8 cm^2 was used in present study.

2.3. Catalyst synthesis

Ni/C and Pd/C catalysts were prepared by an evaporation drying method followed by thermal annealing. The catalyst contained 30 wt % total metal on a carbon support. First, 0.5 g of carbon black (CB, ECP600JD, Lion) was dispersed in deionized water of 0.4 l (>18.2 M cm, Millipore Direct Q 3 UV Water Purification System, Millipore). The aqueous metal nitrate solution made from precursor compound of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Pd}(\text{NO}_3)_2$ (Kishida Chemical) was dissolved in the deionized water containing the carbon black. The slurry contained of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Pd}(\text{NO}_3)_2$ and carbon black was rinsed with deionized water. The powder thus obtained was dried at 100 °C in vacuum for 10 h. Then thermal annealing was performed at 600 °C for 2 h in Ar.

NiPt/C catalyst was prepared by similar method described above. The metal loading on NiPt was selected as 20 wt %. First, 0.5 g of carbon black (CB, ECP600JD, Lion) was dispersed in deionized water of 0.4 l (>18.2 M cm, Millipore Direct Q 3 UV Water Purification System, Millipore). The aqueous metal solution made from precursor compound of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{H}_2(\text{PtCl}_6)$ (Kishida Chemical) was dissolved in the deionized water containing the carbon black. The slurry contained of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{H}_2(\text{PtCl}_6)$, and carbon black was rinsed with deionized water. The powder thus obtained was dried at 100 °C in vacuum for 10 h. Then thermal annealing was performed at 600 °C for 2 h in Ar.

2.4. MEA fabrication

2.4.1. MEA using AEM

A 1 g of Ni/C, a 1 g of Pd/C, a 0.5 g of Pd/C and a 0.5 g of NiPt/C

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