

MnO₂–Pt/C composite electrodes for preventing voltage reversal effects with polymer electrolyte membrane fuel cells

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Abstract

Water is produced at the cathode of proton-exchange membrane fuel cells (PEMFC). If water were not being removed effectively, it would accumulate at the cathode of PEMFC causing the electrode flooding. The consequence is oxygen starvation, thus increasing the concentration overpotential of the cathode. In the worst scenarios, a proton (H⁺) reduction reaction (PRR), instead of the oxygen reduction reaction (ORR), might occur at the cathode. Not only will this cause a cathode potential drop, but the output voltage of a single cell would likely be reversed due to oxygen starvation. This phenomenon is termed the voltage reversal effect (VRE) in this paper. To study and resolve the VRE problem, a MnO₂–Pt/C composite electrode was used to replace the conventional Pt/C electrode. The authors suggest that the electrochemical reduction of MnO₂ in the composite electrode has almost the same Nernstian potential as the ORR, which would serve as a substitute for the ORR in the case of oxygen starvation. Thus, the voltage reversal effect caused by the PRR could be avoided. Two environments, N₂- and O₂-saturated H₂SO₄, were adopted to simulate two cases, i.e., O₂ starvation and O₂ rich. It was found that MnO₂–Pt/C can prevent the voltage reversal effect to a certain extent. In a N₂-saturated 1 M H₂SO₄ solution, the current density of the Pt/C electrode made of 0.6 mg Pt cm⁻² was close to 0, while for the MnO₂–Pt/C composite electrode made of 0.4 mg Pt cm⁻² and 0.8 mg MnO₂ cm⁻², it was as high as 10 mA cm⁻². Though the current generated on the MnO₂–Pt/C composite electrode in the case of oxygen starvation is not as great as that in the case when oxygen rich, it might be high enough for some cases, such as powering a radio, hearing-aid and so like miniature devices. In an O₂-saturated 1 M H₂SO₄, the presence of MnO₂ in a MnO₂–Pt/C composite electrode primarily plays a catalytic role in the ORR. It enhances the catalytic behavior of Pt for the ORR. The impedance spectra of MnO₂–Pt/C and Pt/C electrodes were carried out for the two gases in bubbled electrolyte, which further confirmed that MnO₂ in the composite electrode does substitute for oxygen as an electron-acceptor in the case of oxygen starvation. The discharged MnO₂ can then be restored to its initial state, regardless of whether it is in oxygen rich or starved conditions.

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Keywords: Electrocatalysis; Oxygen electrode; MnO₂; PEMFC

1. Introduction

In contrast to batteries, which are energy storage devices, fuel cells can in principle produce power endlessly as long as fuel and oxidant are fed to the anode and cathode, respectively. Since the only by-products of the electrochemical reaction in a fuel cell are heat and water, fuel cell (FC) technology offers the prospect of zero-emission energy production for applications

ranging from stationary power generation for electrical utilities to urban transportation. The proton-exchange membrane fuel cell (PEMFC) has recently been the focus of intense research and development for powering the next generation of road vehicles, for distributed power generation as well as for powering small portable devices such as cellular phones and laptop computers. Low operating temperatures (ca. 80 °C) and a relatively simple design make the PEMFC a potential candidate for powering the next generation of non-polluting automobiles. The operating principle of a PEMFC is as follows: at the anode, fuel H₂ is oxidized liberating electrons and producing protons. The free electrons flow to the cathode, via an external circuit, where they

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combine with the dissolved oxidant O_2 to produce water and heat.

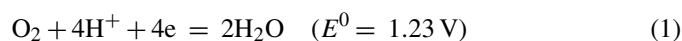
In a PEMFC, hydrogen and oxygen react electrochemically to form water, producing electricity and heat. Several coupled fluid flow, heat and mass transfer processes occur, which have a significant impact on thermal and water management and mass transport limitations. While thermal management is necessary to remove the heat in order to prevent overheating and dehydration of the membrane, proper water management ensures that the membrane remains fully hydrated and therefore maintains good ionic conductivity and hence performance. Thus, two operational issues, (i) thermal and water management and (ii) mass transport limitations, are particularly important. In a typical PEMFC design, the water content is maintained by humidifying the reactant gases. At higher current densities, the excess product water is removed by convection via the air stream, and the rate of removal is controlled by judiciously adjusting the moisture content, pressure drop and temperature in the flow channels.

It is possible that one or more membrane–electrode assemblies (MEAs) in a stack, or even a complete stack in a multi-stack system, will show a reversal in polarity during fuel cell operation. Various circumstances can result in a fuel cell being driven into voltage reversal by other cells in the series stack. Irreversible damage may be caused to the MEAs by such cell reversal incidents. Fuel and oxidant starvation can occur during a sudden change in reactant demand such as start-up and load change [1].

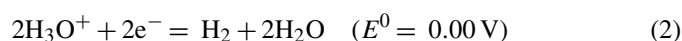
Mass transport limitations are associated with the use of air as the cathodic reactant, and are responsible for a drastic deterioration in performance above a certain current density. This is attributed to the lack of oxygen reaching the catalyst, creating oxygen under-stoichiometry or “starvation” at the cathode. Under steady state conditions, the net mass flow rate of oxygen into the system is equal to the oxygen consumed by the electrochemical reaction. In transient conditions, in particular a step increase in power requirement from the fuel cell, the supply of oxidant to the system lags behind the demand causing a shortage of oxygen and possible local starvation of oxygen for the reaction. An electrical fan tapping power from the fuel cell itself is normally used to ensure that no oxygen starvation occurs [2–4]. Although the fan can solve the problem of oxygen starvation, it dries out the membranes and offsets the improvement in performance due to the power consumption incurred by the fan.

In case excessive water at the cathode is not removed effectively, it would accumulate at the cathode causing the electrode flooding. The consequence is oxygen starvation, thus increasing the concentration overpotential of the cathode. Worse still, a proton (H^+) reduction reaction (PRR), instead of the normal oxygen reduction reaction (ORR), occurs at the cathode.

In the case of oxygen starvation, the ORR



would be replaced by the PRR,

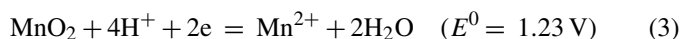


In consideration of the polarization as the current flows through each single cell connected in series in a stack, the output

voltage of a particular single cell that is under oxygen starvation would be likely reversed due to the change of the electrode reaction from the ORR to the PRR. This phenomenon is known as the voltage reversal effect (VRE) in this paper. As long as the VRE appears, the output of the stack will be seriously impaired.

In developing a complete miniaturized power delivery system, where it is possible to operate a fuel cell passively without any active control over the water flow in and out of the device, performance enhancements can be achieved if one is able to move the water within the device from where it is produced in excess to where it is often depleted. At higher current densities, however, the water produced at the cathode can condense and build-up that blocks oxygen transport to the cathode. Particularly in the case where there is no active air movement to enhance the removal of water, the water content at the cathode can build-up until flooding occurs. The problem of flooding is often even greater in methanol fuel cells, where, in addition to the water produced at the cathode, the water from the methanol solution at the anode also crosses over to the cathode. Thus, in order to successfully design a portable fuel cell for electronic devices, the whole system must be taken into consideration. There are many system-level issues to be considered in developing a complete miniaturized power delivery system. These issues include air movement (oxidant supply), fuel delivery, water management, thermal management, power load management and system integration [5–7].

Water management is one of the critical issues to be solved in the design and operation of PEM fuel cells. Especially, in case of small fuel cells operated at room temperature water flooding may appear [4]. If active control of the water management cannot be guaranteed due to size and power demand of auxiliary equipment, passive possibilities of intervention are required. One alternative is to manipulate the characteristic of the used diffusion or backing layers [4,8]. The present work focuses on the VRE caused by cathode flooding. To study and resolve the problem of VRE, a MnO_2 –Pt/C composite electrode is designed to replace the conventional Pt/C electrode. It is based upon the fact that the electrochemical reduction of MnO_2 has almost the same Nernstian potential as ORR as shown below:



The reaction (3) can replace the ORR in the case of oxygen starvation. Thus, the VRE resulted from the PRR could be avoided without the use of a fan to scavenge the excessive water. The objective of this study is thus devoted to resolving this flooding problem with the development of a novel cathode consisting of MnO_2 and Pt/C.

2. Experimental

Electrodes were prepared as described previously [9]. In short, for the measurements described in this study the authors used commercially available catalysts of 40 wt.% Pt/C (Johnson–Matthey) and Electrolytic Manganese Dioxide (EMD) powder widely used in dry battery industries. Carbon cloth (Shanghai Xinxing Carbon Co., China) was used as the

substrate for the supported catalyst. A suspension consisting of catalysts MnO_2 and Pt/C, Nafion solution (diluted to 0.5 wt.%), and iso-propanol was first ultrasonically mixed for about 15 min, then pipetted onto the Teflon-treated carbon cloths and finally heated at 80°C . The electrochemical measurements were conducted in a three-electrode configuration. A saturated silver chloride electrode (SSCE) and a Pt wire electrode were used as the reference electrode and the counter electrode, respectively.

After preparation, the electrodes were immersed in O_2 - or N_2 -saturated 0.05 M H_2SO_4 to simulate the situation of oxygen rich and oxygen starvation, respectively. Current densities are normalized either to the geometric area of the carbon clothes (4 cm^2) or to the Pt-loadings of the electrode. All measurements were conducted at the room temperature (ca. 20°C).

3. Results and discussion

Figs. 1 and 2 show the chronoamperometry of electrodes Pt/C (Fig. 1) with loadings of 0.6 mg cm^{-2} and MnO_2 -Pt/C (Fig. 2) with loadings of 0.4 mg Pt cm^{-2} and $0.8\text{ mg MnO}_2\text{ cm}^{-2}$ in O_2 - and N_2 -saturated 0.05 M H_2SO_4 and subjected to potential jumps from 0.9 to 0.1 V. In the case of oxygen starvation, the cathodic current was almost close to zero for the Pt/C electrode subjected to step potential drops. On the contrary, a considerable

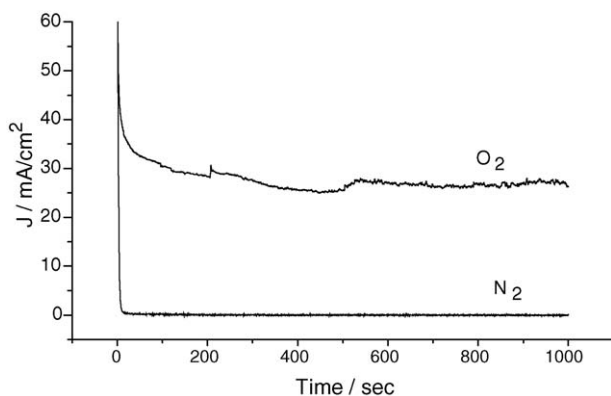


Fig. 1. Chronoamperometry of Pt/C electrode with loadings of 0.6 mg Pt cm^{-2} in O_2 - and N_2 -saturated 1 M H_2SO_4 as the potential jumps from 0.9 to 0.1 V.

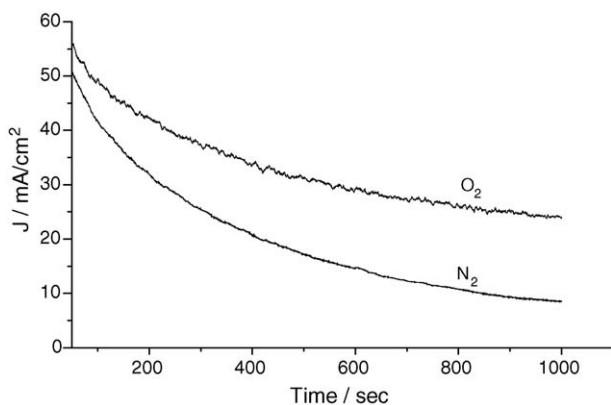
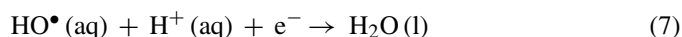
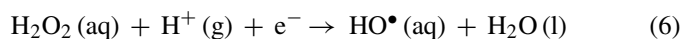
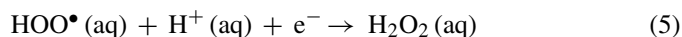
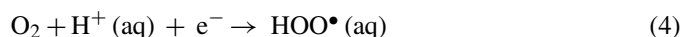


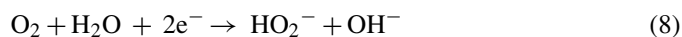
Fig. 2. Chronoamperometry of MnO_2 -Pt/C electrode with loadings of 0.4 mg Pt cm^{-2} and $0.8\text{ mg MnO}_2\text{ cm}^{-2}$ in O_2 - and N_2 -saturated 1 M H_2SO_4 as the potential jumps from 0.9 to 0.1 V.

cathodic current was produced for the composite MnO_2 -Pt/C electrode. Obviously, the cathodic current in the case of oxygen starvation is attributed to reaction (3). In the case of oxygen rich conditions, both the Pt/C and MnO_2 -Pt/C electrodes generated a considerable amount of oxygen reduction current as the potential dropped steeply. Since the current densities are normalized with respect to the Pt-loadings of the electrode, more current was actually obtained from the composite MnO_2 -Pt/C electrode than from the Pt/C electrode as shown in Fig. 3. This implicitly implies that introduction of MnO_2 into the catalyst Pt/C did not only alleviate, to a certain extent, the problem of VRE in the case of oxygen starvation, but also played a synergistic role with Pt/C in the ORR in the case of oxygen rich conditions. This is easily understood because MnO_2 has been used as a catalyst for the ORR [10].

The four one-electron steps in reactions (4)–(7) shown below were studied by calculating the activation energies with one or two additional H_2O molecules coordinated to the transferring proton [11–13]. It was found that the activation energies of reactions (4)–(7) decreased in the sequence of (6) > (4) > (5) > (7). This conclusion coincides with the fact that most of the catalysts only accelerate a two-electron reduction of O_2 to produce H_2O_2 .



The two two-electron transfer processes plus one disproportionation reaction about the ORR on MnO_2 were suggested as follows [14]:



MnO_2 was considered to be a good catalyst for further reduction of HO_2^- [14]. The excellent activity of MnO_2 for the

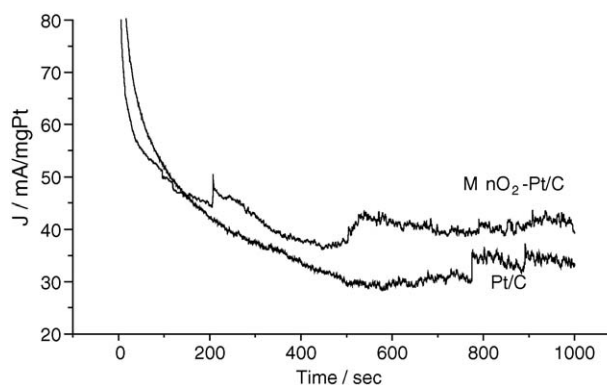


Fig. 3. Chronoamperometry of electrodes Pt/C with loadings of 0.6 mg Pt cm^{-2} and MnO_2 -Pt/C with loadings of 0.4 mg Pt cm^{-2} and $0.8\text{ mg MnO}_2\text{ cm}^{-2}$ in O_2 -saturated 1 M H_2SO_4 as the potential jumps from 0.9 to 0.1 V.

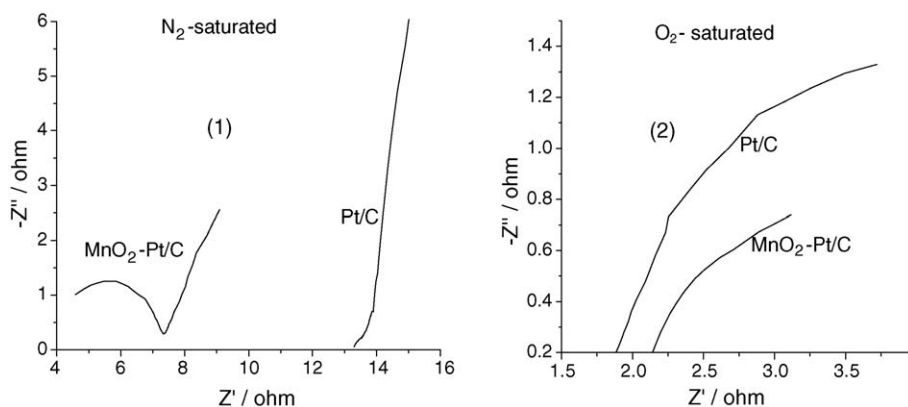


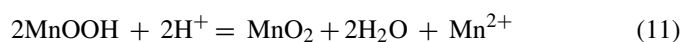
Fig. 4. Impedance spectra at 0.3 V for electrodes MnO₂-Pt/C with loadings of 0.23 mg Pt cm⁻² and 0.46 mg MnO₂ cm⁻² and Pt/C with loadings of 0.3 mg Pt cm⁻² in N₂-saturated (1) and O₂-saturated (2) 1 M H₂SO₄.

reactions (9) and (10) substantially speeds up the ORR at the MnO₂-Pt/C composite electrode.

The impedance spectra of the MnO₂-Pt/C and Pt/C electrodes are shown in Fig. 4 and further confirm the above analysis. The parameters of the equivalent circuit corresponding to the impedance spectra of Fig. 4 are summarized in Table 1. With the introduction of MnO₂ into the Pt/C catalyst, the Faradic reaction resistance in N₂-saturated H₂SO₄ drops from 196 Ω for the Pt/C electrode to 3 Ω for the MnO₂-Pt/C electrode. In O₂-saturated H₂SO₄, no unfavorable result can be observed with the addition of MnO₂ as shown in Table 1. However, excessive MnO₂ would worsen the performance of the composite MnO₂-Pt/C electrode in the case of O₂ rich conditions [15].

According to the experimental results shown above, we can conclude that MnO₂ in the composite electrodes serves the purpose of substituting O₂ for use in case of oxygen starvation. This prompted a question that “can the discharged MnO₂ be restored to its initial state?” If not, the loaded MnO₂ will soon be fully consumed if the starvation persists for a sufficiently long period. In this case, the MnO₂-Pt/C composite electrode would be no different from an ordinary Pt/C electrode. An experiment was therefore designed to elucidate this argument. The composite electrode was first discharged to a certain current in a state of oxygen starvation to a given potential, then the discharge current was interrupted and checked to see if the electrode potential

returned to its value before discharging. The study revealed that the discharged MnO₂ readily recovered to its initial state in an aerated solution [16]. N₂- and O₂-saturated H₂SO₄ electrolytes were alternatively used at the stage of the potential recovery as shown in Fig. 5. The results show that, regardless of the N₂- and O₂-saturated H₂SO₄ electrolytes, the electrode potential rises up very rapidly at first and then gradually climbs to a stable potential close to the open-circuit potential. The difference caused by the types of bubbled gases used is quite small as shown in Fig. 6. The slightly higher recovery potential in the O₂-saturated than in the N₂-saturated H₂SO₄ electrolyte is due to the reaction (1) that imposes a positive potential of 1.23 V on the electrode, thus leading to a higher potential. The rapid rise in potential in the initial stage of the recovery is due mainly to quick adjustment of the electrode/electrolyte interface after the current interruption, as discussed previously [17,18]. The gradual increase in potential during most of recovery time is thought to result from the following two reactions.



The reaction (11) was only taking place on the surface of the MnOOH and should proceed quickly. On the contrary, the reaction (12) is a process in which the protons on the surface of

Table 1
The parameters of the equivalent circuit corresponding to the impedance spectra of Fig. 4

Parameter	N ₂		O ₂	
	Pt-MnO ₂ /C	Pt/C	Pt-MnO ₂ /C	Pt/C
R ₁ (Ω)	4.0 (2.0)	13.0 (0.4)	2.0 (0.3)	1.9 (0.6)
R ₂ (Ω)	3.04 (3.1)	196.04 (13.9)	2.54 (8.1)	2.85 (28.3)
Y ₀	1.2 × 10 ⁻³ (10.7)	2.0 × 10 ⁻³ (3.8)	5.4 × 10 ⁻² (2.8)	1.7 × 10 ⁻² (2.0)
n	0.85 (2.7)	0.89 (1.1)	0.80 (2.8)	0.81 (6.6)
Total error	9.1 × 10 ⁻³	2.4 × 10 ⁻²	1.5 × 10 ⁻²	1.6 × 10 ⁻²

R₁ and R₂ are the electrolyte resistance and Faradic reaction resistance. Y₀ together with n specifies the property of the electrode/electrolyte interface. n ∈ (0, 1); if n = 0, the electrode/electrolyte interface is equivalent to a resistance; if n = 1, a capacitor. Data in parentheses are the relative error of fitting.

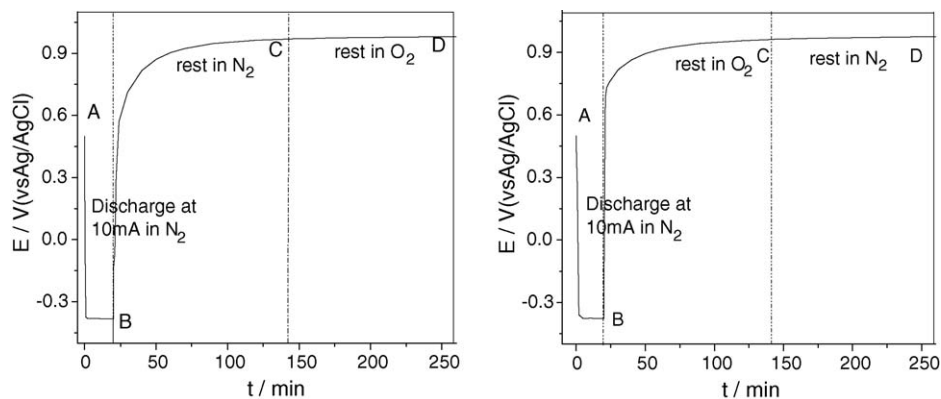


Fig. 5. Chronopotentiometry of $\text{MnO}_2\text{-Pt/C}$ electrode during rest in O_2 and N_2 alternatively saturated H_2SO_4 (segment B–C–D) after discharge at current of 10 mA in N_2 -saturated 1 M H_2SO_4 (segment A–B).

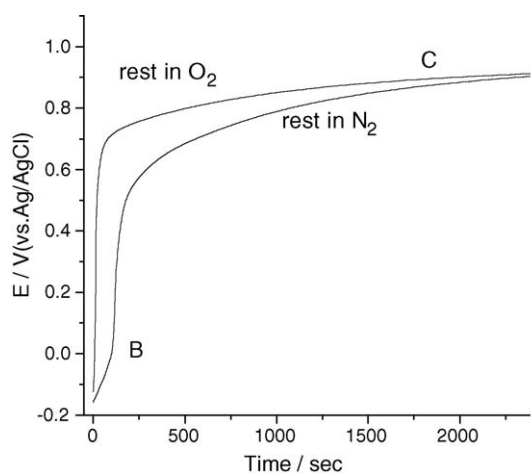


Fig. 6. Superposition of segment B–C in Fig. 5.

the MnOOH diffuse inside the MnO_2 . This process is slow and needs a longer time to complete [19].

4. Conclusions

From the experimental results, the following conclusions can be drawn with respect to the $\text{MnO}_2\text{-Pt/C}$ composite electrodes for limiting the voltage reversal effect with polymer electrolyte membrane fuel cells.

It has been found that $\text{MnO}_2\text{-Pt/C}$ can limit the voltage reversal effect to a certain extent. In a N_2 -saturated 1 M H_2SO_4 , the current density of the Pt/C electrode made of $0.6 \text{ mg Pt cm}^{-2}$ was close to 0 mA cm^{-2} , while for the $\text{MnO}_2\text{-Pt/C}$ composite electrode made of $0.4 \text{ mg Pt cm}^{-2}$ and $0.8 \text{ mg MnO}_2 \text{ cm}^{-2}$, it was as high as 10 mA cm^{-2} . Though the improvement is not great, it might be high enough for some cases, such as powering a radio, hearing-aid and so like miniature devices. It illustrates that the introduction of MnO_2 into the Pt/C catalyst not only can alleviate, to a certain extent, the problem VRE in the case of oxygen starvation, but also play a synergistic role with Pt/C in catalysis of the ORR in the case of oxygen rich conditions.

The impedance spectra of the $\text{MnO}_2\text{-Pt/C}$ and Pt/C electrodes further confirm that MnO_2 in the composite electrode does substitute for oxygen as an electron-acceptor in the case of oxygen starvation. The discharged MnO_2 can recover to its initial state regardless of oxygen rich or oxygen starvation conditions. Thus, it may be possible to apply the proposed composite $\text{MnO}_2\text{-Pt/C}$ electrode for practical use.

Acknowledgements

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