



Short communication

Characterization of MnO₂ positive electrode for Fuel Cell/Battery (FCB)Sunmook Lee^a, Bokkyu Choi^b, Nobuyuki Hamasuna^b, Chihiro Fushimi^a, Atsushi Tsutsumi^{a,*}^a Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan^b Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

ARTICLE INFO

Article history:

Received 23 January 2008

Received in revised form 27 February 2008

Accepted 27 February 2008

Available online 8 March 2008

Keywords:

Manganese dioxide (MnO₂)

Fuel Cell/Battery (FCB)

Fuel cell

Secondary battery

ABSTRACT

The use of manganese dioxide (MnO₂) as a positive electrode material in Fuel Cell/Battery (FCB) systems is described. A positive electrode containing MnO₂ was fabricated and its performance was evaluated for charge/discharge behavior in three different systems: (i) secondary battery positive electrode, (ii) positive electrode in an alkaline fuel cell, and (iii) positive electrode performance in an FCB system by performing half cell tests. MnO₂ was observed to possess redox capabilities as the positive electrode of a secondary battery when it was subject to charge/discharge cycles. It was found that Mn₃O₄, which inhibits the discharge reaction, was produced during charge/discharge cycles. The *I*–*V* characteristics of MnO₂ material were measured to check the feasibility of the fuel cell system by supplying H₂ into the negative electrode and O₂ into the MnO₂ positive electrode, respectively. The MnO₂ electrode showed similar performance to Ni electrode, which was fabricated by using a similar method to the MnO₂ electrode. The MnO₂ electrode also showed that it functioned as an FCB positive electrode, which was confirmed by continued production of current when the O₂ supply was terminated. These results suggest that MnO₂ is a good candidate for an FCB positive electrode material.

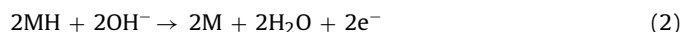
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1. Introduction

Enormous energy demand has led to a search into a wider variety of energy sources. Among others, renewable energy sources such as solar and wind power have been attracting a lot of attention for electric power generation because they are environmentally friendly [1]. However, intermittency and variability of the power production from solar and wind energy result in either excess capacity or lower than desired performance of the energy supply system. Thus, secondary batteries, the most widely employed energy storage system, have been considered as a means to complement such renewable supplies of energy because they exhibit relatively high power output and are rechargeable [2]. However, secondary batteries require further improvements to satisfy and/or accommodate peak power demand [3]. One solution is a hybridization of secondary batteries with fuel cells, called Fuel Cell/Battery (FCB) systems. This hybridized system can function both as a fuel cell and as a secondary battery such that electric power is produced as in a secondary battery when the cells are fully charged. Furthermore, it can also produce electric power by consuming hydrogen and oxygen in a similar way to a fuel cell system when it is completely discharged. The operating principle of an

FCB system is schematically illustrated in Fig. 1. In this system, power is generated by the following fuel cell reactions (Fig. 1a) [4]:

Negative electrode:

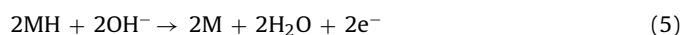


Positive electrode:



where MH is a metal hydride and XO is a metal oxide. At first, hydrogen and oxygen react with the metal electrodes. Metal hydride and metal are produced and stored at the negative and positive electrodes, respectively. Then, the metal hydride reacts with hydroxyl ion at the negative electrode side, generating an electron and metal. At the positive electrode side, reduction of metal oxide takes place, producing metal. This system can also generate power as a battery without feeding hydrogen or oxygen:

Negative electrode:



Positive electrode:



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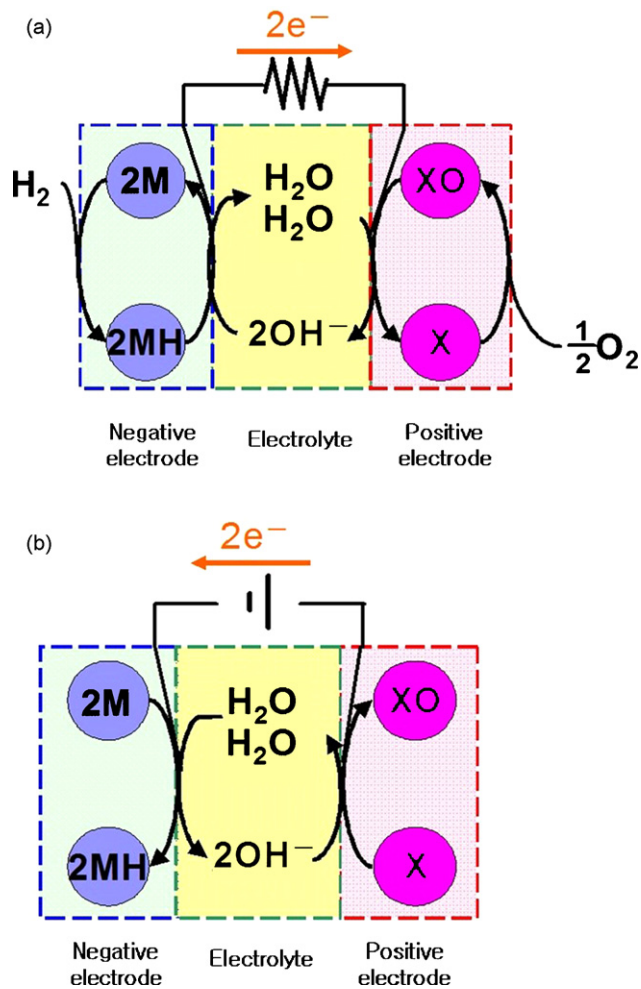


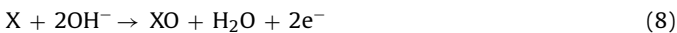
Fig. 1. Operation principle of the Fuel Cell/Battery (FCB) system. (a) Fuel cell (discharge) and (b) secondary battery (charge).

Furthermore, this system can be charged as a secondary battery, in which the following reactions take place as shown in Fig. 1b:

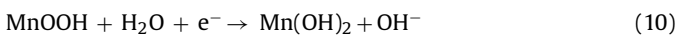
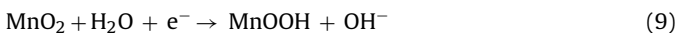
Negative electrode:



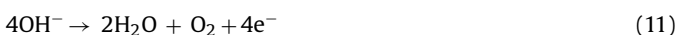
Positive electrode:



MnO₂ is one of the most commonly used positive electrode materials in primary batteries [5], especially electrolytic manganese dioxide (EMD), due to its high activity. The discharge reactions of MnO₂ in basic solution are as follows [6]:



However, MnO₂ has not attracted much attention as a positive electrode material in secondary batteries. This is due to two major reasons: (i) MnO₂ has to compete with the formation of oxygen due to the electrolysis of electrolyte during the charging reaction,



and (ii) MnO₂ converts into electrochemically stable Mn₃O₄ simultaneously with the reduction reaction as follows [7]:

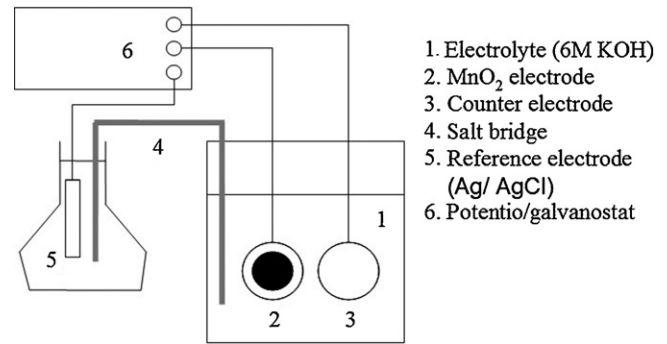
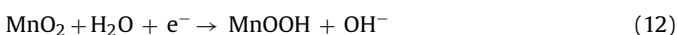
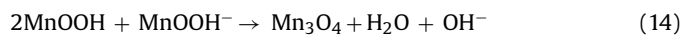
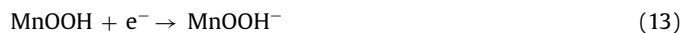


Fig. 2. Schematic diagram of experimental apparatus in the secondary battery test.



Several research groups have reported on the addition of metal and/or metal oxide to MnO₂ electrode in order to overcome these issues [8–12]. Recently, there have been some reports in which this material has been used in rechargeable cells because MnO₂ has reduction capability such as the reduction of hydrogen peroxide (H₂O₂) [9,13]. Furthermore, several studies demonstrated that MnO₂ has an excellent catalytic activity for oxygen reduction [14–16]. Therefore, this study attempted the fabrication of a positive Fuel Cell/Battery electrode with MnO₂ (EMD) and investigated the discharge of the fabricated MnO₂ electrode in an FCB. In this paper, the proof of concept of such a Fuel Cell/Battery is demonstrated.

2. Experimental

2.1. Fabrication of MnO₂ electrodes and battery performance

MnO₂ electrodes were obtained from Kawasaki Heavy Industries, Ltd., where they were fabricated in the following way: First, 700 mg of electrolytic manganese dioxide was mixed with 210 mg of carbon black (CB) as a conductive material. This mixture was added to an aqueous binder solution containing 70 mg of poly(tetrafluoroethylene) (PTFE), and thoroughly mixed until this mixture became homogeneous. Then, 0.1 g of this mixture was coated on a nickel foam (30 mm diameter and 2.0 mm thickness, The Nilaco Corporation) and rolled on both sides, followed by drying in an oven at 110 °C for 30 min. This was then pressed at 6 MPa for 10 min. These fabricated electrodes were subject to charge/discharge cycles for battery performance. A schematic illustration of the discharge experimental setup used for discharge testing is shown in Fig. 2. Discharge performance of the fabricated MnO₂ electrode was investigated by immersing in 150 ml of 6 M KOH and discharging at a rate of 0.2 C (61.6 mAh) g⁻¹-MnO₂. A bare nickel foam with the same size as the MnO₂-painted positive electrode was used as the counter electrode and a Ag/AgCl was used as the reference electrode.

2.2. Fuel cell performance of MnO₂ electrodes

A schematic illustration of the fuel cell setup is shown in Fig. 3. The MnO₂ electrode was fabricated in the laboratory following the same protocols as Kawasaki Heavy Industries, Ltd. The surfaces of MnO₂ positive electrode and the negative electrode (Pt/C-supported, 1 mg-Pt cm⁻²) were immersed in 6 M KOH electrolyte. A Ag/AgCl reference electrode was connected to the main body of KOH electrolyte through a capillary tube filled with saturated KCl in agar gel. The fuel cell performance of the fabricated

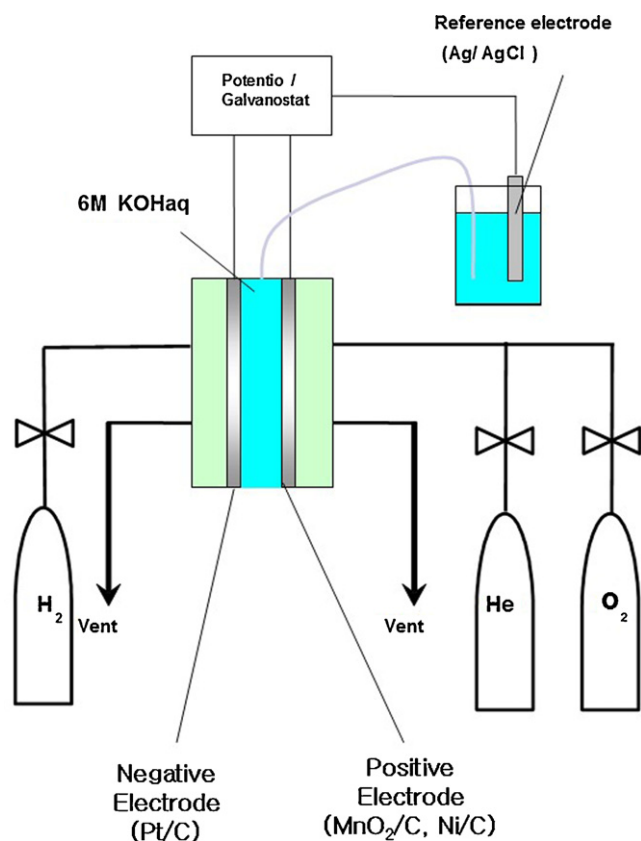


Fig. 3. Schematic diagram of experimental apparatus in the fuel cell test.

MnO₂ electrode was compared with that of the Ni electrode, which was also fabricated in the laboratory with the same method as the MnO₂ electrode. Briefly, 700 mg of nickel (metallic powder) was mixed with 70 mg poly(tetrafluoroethylene) as a binder and 210 mg of carbon black (CB) as a conductive material. The rest of the procedures followed the same protocols as the MnO₂ electrode.

2.3. Electrochemical measurement

The potential–current (*I*–*E*) relation was obtained with Analytical 1480 Multistat (Solartron) at ambient temperature. The current density was increased with 5 mA cm⁻² increment and at 15 min intervals. The electrode potentials were measured versus the Ag/AgCl/saturated KCl reference electrode. All potentials given below are versus this reference electrode.

2.4. X-ray diffraction (XRD)

The crystal structure changes of the electrodes were observed by XRD (XRD miniflex, Rigaku Corporation) at a scan rate of 5° min⁻¹ within 2θ = 20–80°.

3. Results and discussion

3.1. Performance of MnO₂ electrodes

3.1.1. Battery performance

The potential change versus discharge capacity for three successive cycles is shown in Fig. 4. The potential steadily decreased as the electrode discharged, which is typical of a secondary battery electrode. After three charge/discharge cycles, the overall discharge capacity remained almost constant at 110 mAh g⁻¹. However, the

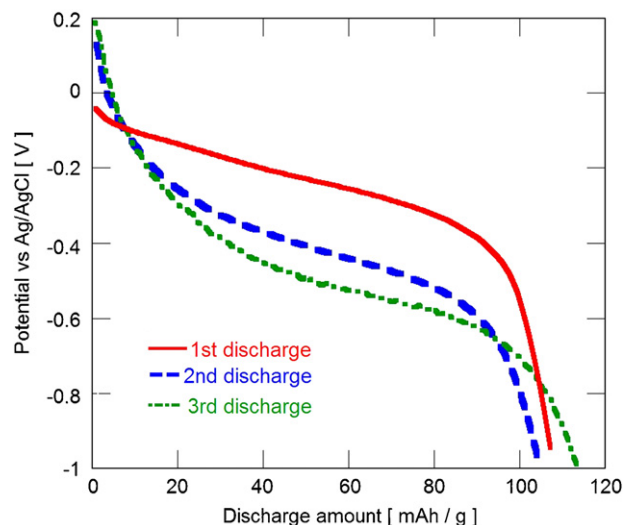


Fig. 4. Galvanostatic discharge voltage profiles of fabricated MnO₂ (EMD) electrodes: 0.2C (61.6 mAh) g-MnO₂.

plateau voltage values of the discharge curves gradually decreased as the number of cycle increased. XRD patterns of the MnO₂ electrode were compared before and after the charge/discharge experiment as shown in Fig. 5. The XRD patterns indicated that there were additional peaks after the charge/discharge cycle, which are assigned to Mn₃O₄. It is known that Mn₃O₄ inhibits the recharge reactions of MnO₂ due to its stable spinel structure and thus could decrease the discharge performance of the positive electrode (EMD) on subsequent discharge cycles because of incomplete recharging [17]. Therefore, the observed decrease in discharge capacity with cycling is attributed to the formation of Mn₃O₄. This change in crystalline structure induces the gradual decrease in the plateau voltage values of the discharge curves in Fig. 4.

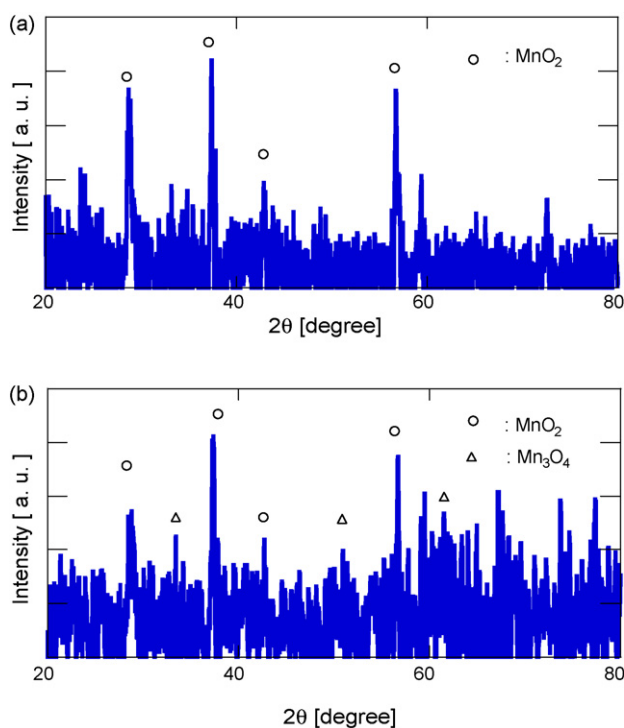


Fig. 5. X-ray diffraction (XRD) patterns of EMD electrode for: (a) before charge/discharge cycles and (b) after three charge/discharge cycles.

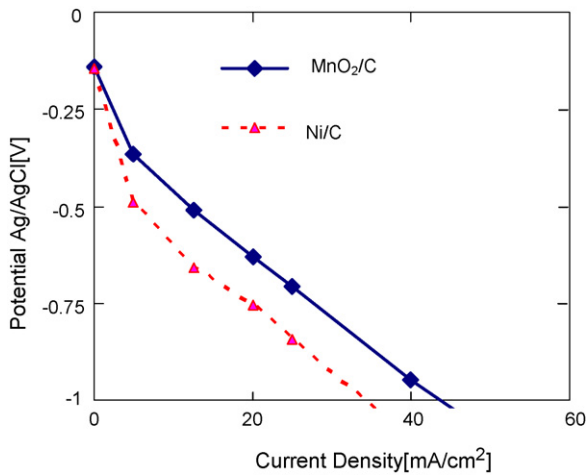


Fig. 6. I - V polarization curves of EMD and nickel positive electrodes in fuel cell mode. H_2 and O_2 were supplied to the negative and positive electrodes at a rate of 150 ml min^{-1} (0.2 MPa, 298 K), respectively.

3.1.2. Fuel cell performance

MnO_2 has been widely used as a positive electrode material [5,7], but it has also been known to have a high catalytic activity for oxygen reduction as well [14–16]. The current–voltage characteristics of MnO_2 electrodes are shown in Fig. 6. H_2 and O_2 were continuously supplied to the negative electrode and positive electrode, respectively. In Fig. 6, the performance of MnO_2 electrode is also compared with that of the Ni electrode, which is a commonly used positive electrode in alkaline fuel cell (AFC) [18]. The sweep was stopped at -1.0 V because H_2O begins to evolve H_2 below -1.0 V . The I - V curves indicate that MnO_2 has a similar reduction capability to Ni. It can, therefore, be concluded that MnO_2 was also feasible to use as a positive electrode in alkaline fuel cell systems.

3.2. Performance under cycled charge/discharge conditions in FCB system

Half cell performance of a Ni positive electrode subjected to intermittent discharge in an alkaline FCB system is shown in Fig. 7. O_2 was initially supplied for 60 s, which was followed by the shut-

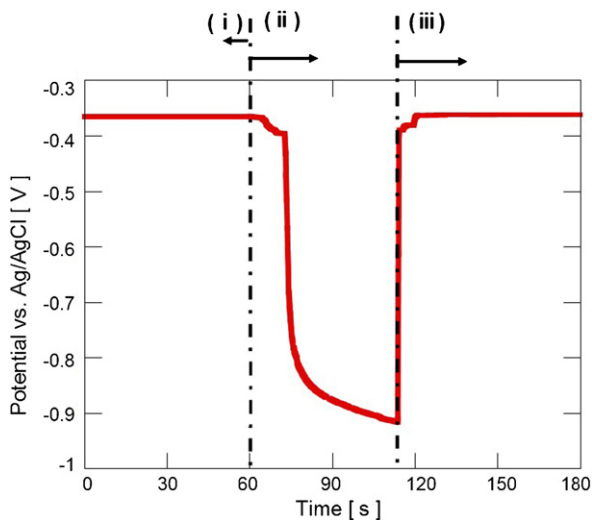


Fig. 7. Potential behavior of Ni electrode under galvanostatic discharge: (i) O_2 was supplied; (ii) O_2 supply was shut off; and (iii) O_2 was re-supplied.

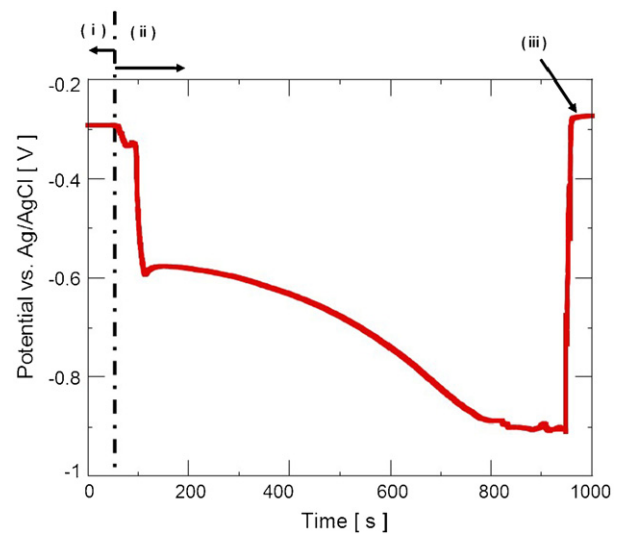


Fig. 8. Potential behavior of EMD electrode: (i) O_2 was supplied; (ii) O_2 supply was shut off and discharge started at a discharge current of 1.31 mA cm^{-2} ; and (iii) O_2 was re-supplied.

down of the O_2 supply for 50 s. During the shutdown period, the potential decreased to -0.9 V , at which time O_2 was immediately re-supplied to the system. It was observed that the potential decreased drastically when the O_2 supply was shut off, which is a typical I - V behavior of fuel cell electrodes and occurs due to the electrolysis of water. In contrast to the Ni positive electrode, one of the most prominent advantages of the hybrid FCB system with MnO_2 positive electrode is that the cell is able to produce electric power even when O_2 supply is shut off. In order to investigate this aspect, potential changes were measured under both O_2 supply and shut-off conditions. Fig. 8 shows the potential changes of the EMD electrode when there is a change in the O_2 supply conditions. O_2 was initially supplied for 60 s, which was followed by the shutdown of the O_2 supply for 880 s. The potential declined slowly from approximately -0.6 to -0.9 V over a period of approximately 850 s, at which time O_2 was re-supplied into the system. For the initial 60 s, the system maintained a stable potential of approximately -0.29 V because of the O_2 supply, indicating it was working as a fuel cell. When the supply of O_2 was shut off, there was a drastic reduction in the potential for a few seconds, followed by the gradual decrease in the potential, representing a typical battery discharge. This result indicates that the FCB system was functioning as a battery during the shutdown of the O_2 supply. In addition, when O_2 was re-supplied after the discharge, the potential was found to be fully recovered. It can be concluded that the EMD electrode can function not only as a positive electrode in secondary batteries when it is charged, but also as a catalyst in a positive electrode of fuel cell systems when it is fully discharged and O_2 is supplied.

4. Conclusions

A positive electrode containing MnO_2 was fabricated and tested for the proof of concept of a hybrid system, called a Fuel Cell/Battery (FCB). It was observed that MnO_2 possesses redox capabilities as a positive electrode of a secondary battery when it is subject to charge/discharge cycles. The I - V characteristics of MnO_2 material were measured to investigate the feasibility of operating the MnO_2 electrode in fuel cell mode by supplying H_2 into the negative electrode and O_2 into the positive electrode, respectively. Under these conditions (fuel cell mode) the MnO_2 positive electrode showed similar performance to the fabricated Ni positive electrode. The half

cell performance was evaluated under charge/discharge conditions created by periodically interrupting the O₂ supply, which indicates that the fabricated cell is able to produce power even when O₂ supply is shut off, which is one of the most prominent advantages of this system.

Acknowledgements

Insightful suggestions and support from Dr. Kazuo Tsutsumi at Kawasaki Heavy Industries, Ltd. are greatly appreciated. The authors gratefully acknowledge the financial support from the Grant-in-Aid for Scientific Research (B) (number 19360434) by the Japanese Society for the Promotion of Science (JSPS).

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