



Hanging meniscus configuration for characterizing oxygen-reduction electrocatalysts in highly concentrated electrolytes

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ABSTRACT

Oxygen reduction reaction (ORR) in metal-air batteries or fuel cells often require highly concentrated electrolyte for higher conductivity and electrochemical stability. However, conventional rotating disk electrode (RDE) method is ineffective to evaluate ORR activity in the real systems, because the scarce dissolved oxygen in highly concentrated electrolyte fails to provide significant ORR on RDE. Herein, we report a hanging meniscus configuration method for evaluating the electrocatalytic activity in highly concentrated electrolyte solutions, utilizing atmospheric oxygen through the triple-phase boundary. The newly developed method evaluated the ORR activity of silver and platinum catalysts in highly concentrated KOH electrolyte for zinc-air batteries, enabling the characterization in more realistic experimental condition.

1. Introduction

As represented by the Paris Agreement in 2015, the global society is striving toward a clean and green future. Advanced fuel cells and metal-air batteries can effectively utilize and store renewable energy, providing reliable solutions to air pollution and global warming [1–3]. In this context, the oxygen-reduction reaction (ORR) plays a vital role as the cathodic reaction in these energy-storage and conversion devices [4], and many researchers have sought more efficient ORR catalysts based on precious [5–9] or non-precious metals to address this pivotal issue [10–17]. To obtain more efficient catalysts, it is essential to develop a reliable platform to evaluate the catalysts, particularly to accelerate the screening process.

The electrochemically active surface area (ECSA), which is the contact area between the catalyst and electrolyte, is an indispensable descriptor for highly efficient catalysis [18,19]. ECSA is often evaluated using underpotential deposition of proton with cyclic voltammetry, or using the limiting current of ORR in a rotating disk electrode (RDE) configuration. The RDE method requires sufficient amount of dissolved oxygen as the RDE is completely immersed in the electrolyte solution. And conventional RDE method fails to characterize ORR catalysts in practical electrolytes because the oxygen solubility rapidly drops at concentration significantly higher than 1.0 M [20]. As a

result, in real-world devices, such as fuel cells or metal-air batteries, the triple-phase boundary (TPB) is a more direct criterion for the efficient reduction of atmospheric oxygen [21,22]. The TPB is a measure of the boundary where O₂ (gas), e⁻ (solid), and ions (liquid) interact. Therefore, a practical platform for characterizing the TPB as well as ECSA of ORR catalysts is highly desirable.

Herein, we present a method for characterizing the TPB of porous ORR catalysts using a hanging meniscus configuration (HMC; Fig. 1), which has been mainly utilized for the fundamental electrochemistry of single-crystalline electrodes [23–30]. The HMC method provides a proper condition for the formation of the TPB, as it interconnects the pathways of the electrons (carbon fibers), ions (electrolyte), and oxygen (air). As a result, the entire catalytic surface that is in contact with the electrolyte provides the TPB in the hanging meniscus configuration. Since this method does not require hydrodynamic instrumentation, it is cost-effective and convenient for ORR catalyst evaluation. At the same time, HMC method is capable of characterizing ORR catalysts in highly concentrated electrolytes where conventional RDE method fails due to the low dissolved oxygen, because atmospheric oxygen is reduced in HMC method in contrary to the RDE method that mainly reduces the dissolved oxygen in the electrolyte solution. When it was applied to a practical zinc-air battery system, the HMC method

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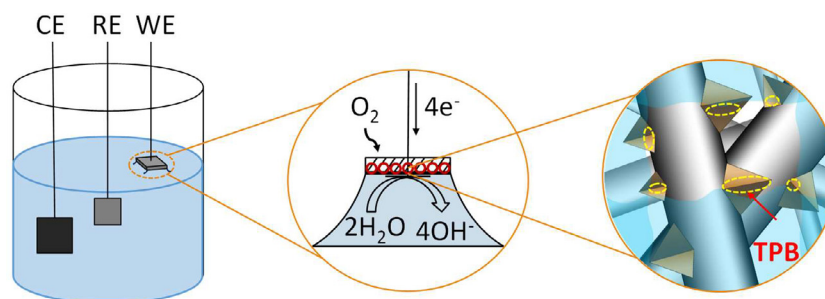


Fig. 1. Schematic of the hanging meniscus configuration system.

reduced the complexity of the characterization processes, thereby enhancing reliability and efficiency.

2. Experimental

2.1. Material synthesis

2.1.1. Electrodeposition of Ag and Pt onto glassy carbon of RDE electrode

The ORR activity of the air catalysts was analyzed by conventional rotating disk electrode (RDE; AFMSRCE; PINE Co.) method. The Pt and Ag catalysts were individually electrodeposited on the glassy carbon of RDE electrode with an exposed area of 0.1963 cm^2 . To this end, a two-electrode cell was equipped with glassy carbon of RDE electrode as the working electrode (WE) and activated carbon cloth (ACC; ACC-5092-20, Kynol Co.) as the counter electrode (CE). A positive current of $+40 \text{ mA}$ was applied up to the total charge 1 C cm^{-2} . Then Nafion solution (5 wt% in aliphatic alcohol; Sigma Aldrich) was drop-casted for stronger binding of the electrodeposits, followed by drying under an infrared (IR) lamp for 10 min.

2.1.2. Electrodeposition of Ag onto carbon paper

Porous Ag/C electrocatalytic electrodes were prepared by electrodeposition of Ag onto a porous carbon paper (C; JNTG70H, JNTG Co.) substrate in a two-electrode configuration using 0.05 M AgNO_3 (99.8%, Aldrich Co.) as the electrolyte and ACC as CE. Ag was anodically electrodeposited onto C by applying $+40 \text{ mA}$ current up to a total charge of 1 C cm^{-2} , followed by washing with deionized (DI) water and drying under an IR lamp for 10 min. Finally, a PTFE (60 wt%, Sigma-Aldrich) coating was done on one side of the Ag/C electrocatalyst to make it hydrophobic. For this, a $40 \mu\text{L}$ of 30 wt% PTFE dispersion in DI water was spread on a glass plate using a pipette, and one side of the Ag/C electrocatalytic electrode was placed on the PTFE dispersion. Afterwards, the PTFE-coated Ag/C electrocatalyst was dried under vacuum at 100°C for an hour.

2.1.3. Loading commercial Pt/C catalyst onto the carbon paper

20% platinum on carbon (Pt/C; Alfa Aesar), isopropyl alcohol, and nafion were taken in the ratio of 10:10:1, respectively, in a 10 mL glass vial and kept under sonication for 1 h. The above solution was then drop-casted onto the carbon paper using a micropipette followed by drying at 120°C for 1 h.

2.2. Electrochemical measurements

2.2.1. Preparation and characterization of electrolytes

The electrolytes were aqueous solutions of (i) 1.0 M KOH (85%; Daejung Co.), (ii) $1.0 \text{ M KOH} + 0.02 \text{ M ZnO}$ (99.9%, Aldrich Co.), and (iii) $8.5 \text{ M KOH} + 0.31 \text{ M ZnO}$. In this work, ZnO serves as the source of zinc ions for the zinc-ion batteries application; considering the significantly less solubility compared to KOH, it is highly probable that the effect on the O_2 solubility is insignificant. In general, the sol-

ubility of ZnO depends on KOH concentration; while 8.5 M KOH solution can dissolve ZnO up to 0.31 M , the solubility is only 0.02 M for 1.0 M KOH . The conductivity measurements of the electrolytes were performed using a conductometer (Lab 955; SI Analytics Co.; after nonlinear temperature compensation to the value at 25°C reference temperature), which was calibrated using 0.01 M KCl solution (cell constant = 479 cm^{-1}). Viscosity measurements were conducted using a viscometer (HR-20 rheometer, TA instrument Co.). The ionic conductivity and viscosity values for the different electrolytes are listed in Table 1. In overall, the electrolytes' viscosity was $15 \sim 18$ times larger than that of deionized water. And the ionic conductivity of 8.5 M KOH electrolyte was ca. 2.6 times larger than that of 1.0 M KOH electrolyte. For the same KOH concentration, adding ZnO led to slightly less ionic conductivity and viscosity.

2.2.2. ORR characterization in the RDE configuration

The cell was constructed with the RDE electrode as WE, and two Zn foils (99.9%, 0.25 mm thick, Alfa Aesar Co.) as the counter electrode (CE) and reference electrode (RE), respectively. The electrolyte was purged with O_2 gas for 30 min before the initiation of the experiment and continued until the end of the RDE measurements. Potential was linearly scanned from 1.5 to 0.5 V vs Zn/Zn^{2+} at 5 mV s^{-1} .

2.2.3. ORR characterization in the hanging meniscus configuration (HMC)

We implemented the hanging meniscus configuration of the working electrode by hanging the porous catalyst substrate ($1 \text{ cm} \times 1 \text{ cm}$) in-plane on the surface of the electrolyte using a Pt wire; and Zinc foils were immersed in the electrolyte as counter ($1 \text{ cm} \times 1 \text{ cm}$) and reference ($0.5 \text{ cm} \times 1 \text{ cm}$) electrodes as demonstrated in Fig. 1. The volume of the electrochemical cell was 100 mL , and the approximate volume of electrolyte was 50 mL . The electrolytes used were aqueous solutions of (i) $8.5 \text{ M KOH} + 0.31 \text{ M ZnO}$ and (ii) $1.0 \text{ M KOH} + 0.02 \text{ M ZnO}$. A meniscus was formed at the electrolyte surface, with the PTFE-coated side of the catalyst facing atmospheric air. Cyclic voltammetry was conducted in the potential range of $1.0 \sim 1.9 \text{ V}$ vs Zn/Zn^{2+} at 1 mV s^{-1} .

2.2.4. Fabrication of zinc-air rechargeable cells

We built two different types of zinc-air rechargeable cells: a four-electrode cell in the hanging meniscus configuration and a two-electrode cell using the sandwich configuration.

2.2.4.1. Four-electrode cell. The four-electrode configuration includes two working electrodes for oxygen reduction (WE_1 , PTFE coated Ag/C or Pt/C catalytic electrode in a hanging meniscus configuration, 1 cm^2) and oxygen evolution (WE_2 , stainless steel mesh, SS316L, McMaster Co., 1 cm^2). The electrolyte was $8.5 \text{ M KOH} + 0.31 \text{ M ZnO}$ aqueous solution. And Zn foils in dimensions of $1.0 \text{ cm} \times 0.5 \text{ cm}$ and $1.0 \text{ cm} \times 1.0 \text{ cm}$ were RE and CE, respectively. Two potentiostat channels were synchronized in such a way that discharging and charging could be performed separately on WE_1 and

Table 1

Ionic conductivity and viscosity of the electrolytes used.

Electrolyte	Ionic conductivity (mS cm ⁻¹ at 25 °C)	Viscosity (cP)
8.5 M KOH	618	18.5
8.5 M KOH + 0.31 M ZnO	590	17.2
1.0 M KOH	225	15.7
1.0 M KOH + 0.02 M ZnO	220	15.2

WE₂, respectively. The charge/discharge cycling cut off was fixed to 2 mAh cm⁻² at varied current density.

2.2.4.2. Two-electrode full cell. The two-electrode zinc-air secondary full cell was fabricated by using PTFE-coated Ag/C or Pt/C catalytic electrode (2.0 cm²) as the WE and a Ni gauze (2.0 cm²; 100 mesh woven wire, 0.1 mm diameter, Alpha Aesar Co.) as the anode substrate. The apparent area was 2.0 cm² for both electrodes. The cells were fabricated without separator; and the approximate distance between positive and negative electrodes was 2.0 mm. PTFE-coated carbon paper served as the gas diffusion layer as well as the substrate for the electrocatalytic layer. The electrolyte was an aqueous mixture of 4 M KOH (85.0%, Junsei Co.), 0.1 M ZnO (zinc source; 99.0%, Junsei Co.), and 3 mM SnO (to suppress the dendritic growth; 99.9%, Alfa Aesar Co.), saturated with 0.5 g Ca(OH)₂·2Zn(OH)₂·2H₂O (calcium zincate; scavenger for Ca(OH)₂ and Zn(OH)₄²⁻) as an additive for stable operation of secondary zinc-air cells.

3. Results and discussion

Conventional RDE method provided normal hydrodynamic voltammograms of ORR in a marginally concentrated electrolyte of 1.0 M KOH [31], with the maximum dissolved oxygen of 0.84 mM [32], as shown in Fig. 2a and b. The half-wave potential of the Pt/C and Ag/C catalysts were 1.22 V and 1.06 V vs Zn/Zn²⁺, respectively, evidencing the superior ORR kinetics of Pt/C over Ag/C. The Pt/C catalyst produced a limiting current of -6.88 mA cm⁻², which was approximately 2.52 times that of Ag/C. However, both catalysts showed negligible ORR activities in a highly concentrated electrolyte of 8.5 M KOH saturated with ZnO (Fig. 2c and d), where the oxygen solubility is ca. 0.041 mM [32], in accordance with the previous report [20].

On the other hand, the HMC method evaluates ORR in the highly concentrated electrolyte of 8.5 M KOH that is saturated with ZnO, overcoming the limitations of the RDE method. This is because the HMC method directly utilizes the atmospheric oxygen, while the RDE method depends on the lean dissolved oxygen in the electrolytes. In the hanging meniscus configuration, both catalysts exhibited similar onset potentials for ORR: 1.37 V and 1.34 V vs Zn/Zn²⁺ for Pt/C and Ag/C, respectively, in 8.5 M KOH + 0.31 M ZnO electrolyte (Fig. 3a and b). However, the ORR activity of Pt/C was severely degraded by cycling, because of the loss of electronic contact between Pt nanoparticles and the carbon substrate in highly concentrated alkaline electrolytes [33–35]. Conversely, the ORR activity of Ag/C increased upon repeated cycling and achieved saturation at -4.06 mA cm⁻² and -1.95 mA cm⁻² in 8.5 M KOH and 1 M KOH electrolytes (both saturated with ZnO), respectively (Fig. 3b–d). From Faraday's law,

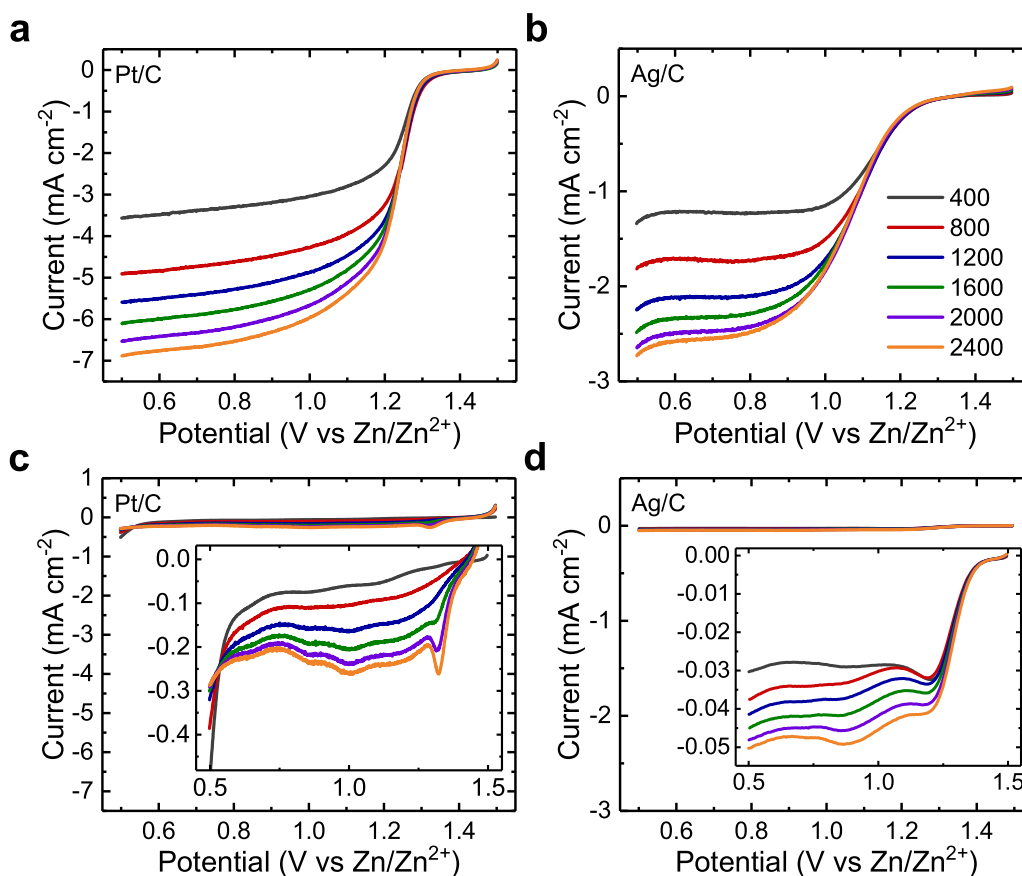


Fig. 2. RDE results of the (a) Pt/C and (b) Ag/C catalysts in a 1.0 M KOH electrolyte; RDE results of the (c) Pt/C and (d) Ag/C catalysts in 8.5 M KOH + 0.31 M ZnO aqueous electrolytes. Scan rate was 5 mV s⁻¹ for the voltammograms. The numbers of the legends stand for the rpm values.

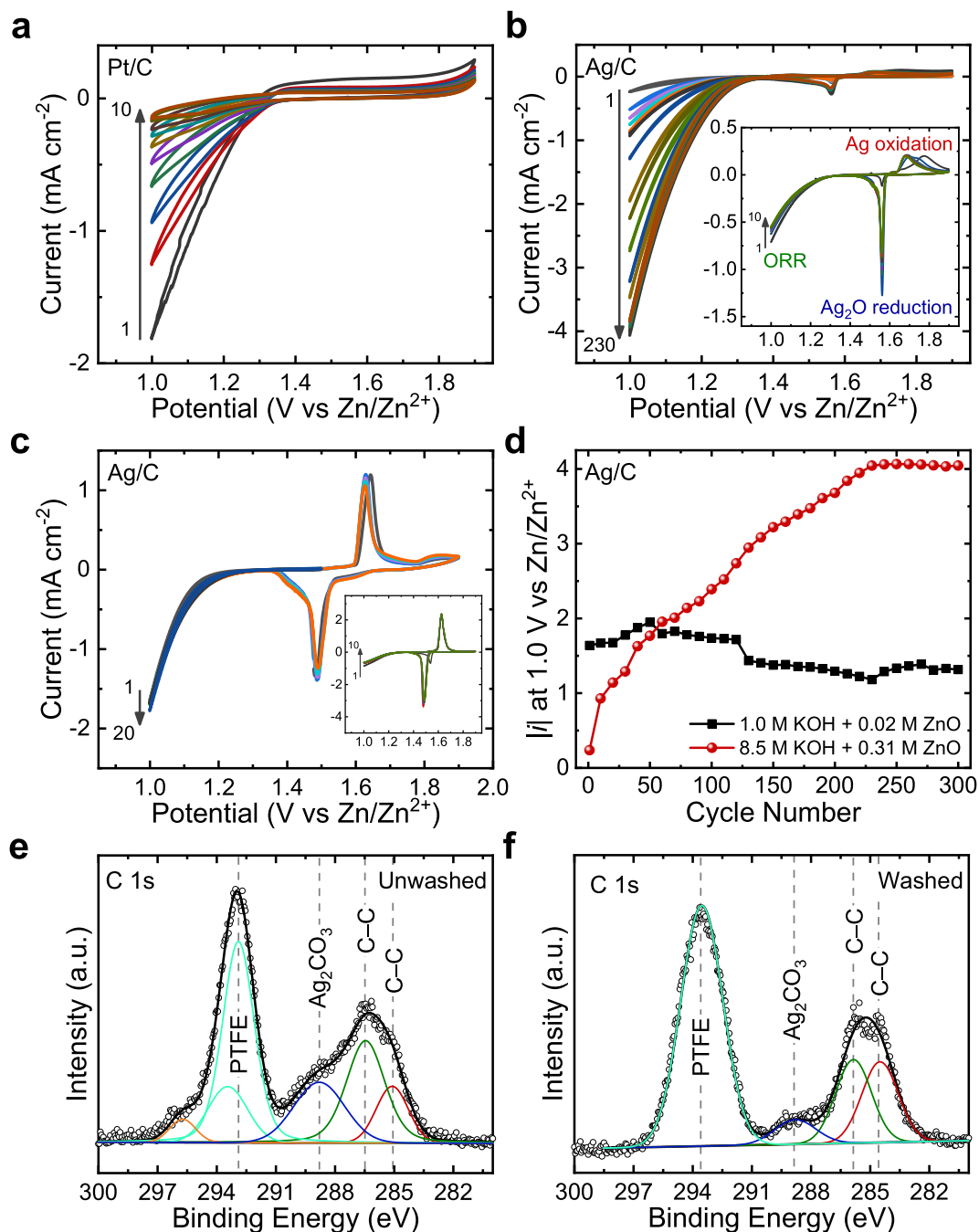


Fig. 3. ORR analysis of (a) Pt/C and (b) Ag/C catalysts in highly concentrated 8.5 M KOH and 0.31 M ZnO aqueous electrolytes, and (c) Ag/C in 1.0 M KOH and 0.02 M ZnO aqueous electrolyte by the hanging meniscus configuration method. (d) ORR current density with respect to the cycle number. C 1s XPS spectra of Ag/C after the initial cycling, (e) unwashed and (f) washed with DI water. Scan rate was 1 mV s^{-1} for the voltammograms.

the current density of 4.06 mA cm^{-2} corresponds to the rate of O_2 reduction of $336.6 \text{ ng O}_2 \text{ cm}^{-2} \text{ s}^{-1}$ or $236 \text{ nL O}_2 \text{ cm}^{-2} \text{ s}^{-1}$. The superior ORR activity in 8.5 M KOH for HMC method may be attributed to the less flooding of the carbon paper substrate due to the higher viscosity compared to 1.0 M KOH electrolyte solution. It is noted that we chose slower scan rate of 1 mV s^{-1} for the HMC experiments to ensure sufficient O_2 diffusion from the atmospheric air. On the other hand, higher scan rate of 5 mV s^{-1} was used for the RDE experiments to save measurement time, because limiting current is not affected by the scan rate under the hydrodynamic condition.

Notably, a washing step is necessary for the Ag/C catalyst to attain such a high ORR activity. Before washing, the ORR activity remained at -0.6 mA cm^{-2} attributable to the formation of a silver carbonate

(Ag_2CO_3) passivation layer, as shown in the inset of Fig. 3b. However, following the initial cycling for several cycles, subsequent washing with deionized water and drying under an infrared lamp for 10 min led to a substantial enhancement in the ORR activity upon the reiteration of the cyclic voltammetry. To understand the enhancement by washing after the initial cycling, we analyzed the samples using X-ray photoelectron spectroscopy (XPS). Upon the initial cycling, a significant amount of Ag_2CO_3 was formed on the surface of the Ag/C catalyst layer, as shown in Fig. 3e. Conversely, most of the peaks disappeared after washing and drying the catalyst layer (Fig. 3f). Considering the XPS analysis, Ag_2CO_3 may have blocked the gas-diffusion pathways during the initial cycling; thus, there was not enough TPBs for the ORR. However, the washing process removed a significant

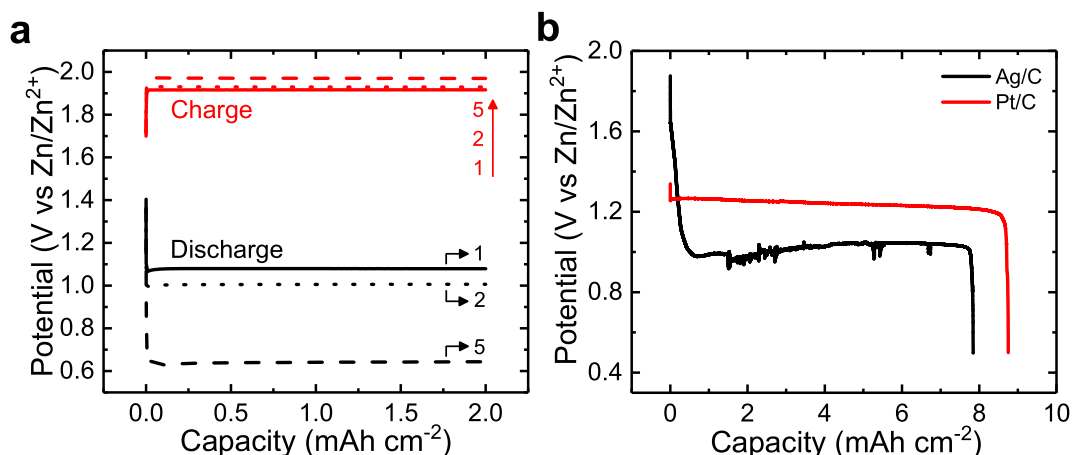


Fig. 4. Zinc-air secondary cell investigations of the Ag/C catalyst using (a) 4-electrode and (b) 2-electrode configurations. The numbers in (a) specify the current density in mA cm^{-2} , and the current density was 1.0 mA cm^{-2} for (b).

amount of the excess Ag_2CO_3 layer, providing sufficient gas-diffusion pathways, while the remaining thin film of Ag_2CO_3 acts as a passivation layer that prevents further formation of Ag_2CO_3 on the carbon surface.

Fig. 4a shows the voltage profiles of a rechargeable zinc-air secondary cell at various current densities using the Ag/C catalytic electrode in a hanging meniscus configuration. A stable cycle performance for up to 30 cycles was achieved, as evidenced by the consistent voltage profiles. The voltage difference between charging (oxygen evolution reduction) and discharging (ORR) is ca. 0.9 V, which is analogous to those of general metal-air batteries. The overpotential for ORR increased from 0.3 to 0.8 V as the current increased from 1 to 5 mA cm^{-2} . Regardless of the overpotential, the discharge potential was over 1.0 V vs Zn/Zn^{2+} , at up to 2 mA cm^{-2} , which is a fairly high rate for metal-air batteries. Such stable operation together with the high-rate capability of the full cells reaffirms the excellent ORR activity of the Ag/C electrodes in the chemical environment of practical zinc-air batteries. Fig. 4b shows the discharge-voltage profiles of zinc-air battery full cells at 1 mA cm^{-2} in a more practical two-electrode configuration. The Zn metal was not incorporated in the beginning but was deposited during the charging of the cell, following the ‘anodeless’ battery concept. For Ag/C catalytic electrode, the average discharge voltage was $\sim 1.0 \text{ V}$ and the areal capacity was ca. 7.84 mAh cm^{-2} ; these values were comparable to the discharge voltage of $\sim 1.2 \text{ V}$ and areal capacity of 8.75 mAh cm^{-2} for commercial Pt/C catalyst. It is noted that the Ag/C catalytic electrodes were conditioned by the same washing process under the hanging meniscus configuration, before fabricating all the above rechargeable cells.

4. Conclusion

We developed a reliable, cost-effective, and convenient hanging meniscus configuration method for characterizing porous electrocatalysts in practical highly concentrated electrolytes, in which the conventional RDE method fails because of the lack of dissolved oxygen. The hanging meniscus configuration method enables a more complete evaluation of TPB and optimization of the porous catalyst layer, supplementing the RDE method that mainly evaluates ECSA and inherent activity.

CRedit authorship contribution statement

Ji Su Kim: Investigation, Writing – original draft, Investigation. **Sangram Keshari Mohanty:** Investigation, Writing – original draft. **Sol Jin Kim:** . **Kyeongmin Moon:** Investigation. **Jiung Jeong:** Inves-

tigation. **Ki Young Kwon:** Investigation. **Heon-Cheol Shin:** Supervision. **Kang Hyun Park:** Supervision. **Hyun Deog Yoo:** Conceptualization, Methodology, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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