Electrocatalytic Activity of Reduced Graphene Oxide Supported Cobalt Cinnamate for Oxygen Evolution Reaction

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Abstract: The stability of porous coordination polymers during an electrochemical reaction could be improved by introducing supporter materials. An $\text{I}_3\text{O}_0$-type inorganic hybrid electrocatalyst, cobalt cinnamate, supported on reduced graphene oxide (rGO) was successfully prepared for an oxygen evolution reaction. The electrocatalytic activity and stability of cobalt cinnamate(catalyst)/rGO composite were significantly improved due to the strong interaction between catalyst and supporter, which led to enhanced anchoring stability and electrical conductivity. The catalyst/rGO composite shows ~30 mV reduction in overpotential and improvement in durability from $\geq 35\%$ to $\geq 70\%$ after a reaction time of 12 h, compared to the catalyst alone.

Keywords: oxygen evolution reaction; electrocatalyst; porous coordination polymers; metal-organic frameworks; graphene oxide composite

1. Introduction

Over recent decades, substituting conventional fossil fuel-based energy systems has attracted tremendous attention owing to the depletion of fossil fuels and the environmental problem. In the energy field, a water splitting reaction, such as oxygen evolution reaction (OER), is one of the critical steps for efficient energy conversion/storage systems [1–3]. However, sluggish kinetics of OER due to the massive amount of energy consumption during the cleavage of O-H bond and formation of O-O bond leads to high overpotentials and thus requires the use of catalysts to make the reaction feasible [4]. The noble metal catalysts based on Ir or Ru are well known as the best electrocatalysts for OER, but they have high prices and scarcity problems [5,6]. Therefore, it is urgent to develop low-cost, efficient, and non-noble metal electrocatalysts.

Porous coordination polymers (PCPs), known as metal-organic frameworks (MOFs), are an important class of porous solid materials due to their wide range of application [7,8]. PCPs have attracted attention for many applications, especially as electrocatalysts due to their distinctive properties including large surface area, porosity, catalytically active transition-metal centers, and tunable structures [9,10].

Many PCPs have been considered as promising candidates for electrocatalytic catalysts [11–13]. Until now, however, such research has been focused only on the MOFs classified as $\text{I}_0\text{O}^3$-type, where “I” and “O” represent the dimensionality of the inorganic M-O (metal-oxygen) connectivity and the M-L (metal-ligand) connectivity in the organic component, respectively [14]. As the dimensionality of inorganic connectivity (I) increases, the structures possess higher dimensionality of M-O-M bonds, and then phenomena such as magnetism and conductivity can be expected. Recently, we reported the $\text{I}_3\text{O}_0$-type porous cobalt cinnamate hybrid compound and its efficient electrocatalytic activity for OER [15]. The structure of the cobalt cinnamate shows a non-interpenetrating diamon-
doid topology of its CoO$_4$ network (3D extended Co-O-Co inorganic block) decorated by π-conjugated cinnamate.

For the electrochemical application, catalysts should be properly introduced onto the electrode surface. The electrical contact between the electrode surface and the catalyst is one of the critical points for electrocatalytic performance because it affects the efficiency and durability of the electrocatalyst. Many materials used as supporters have been widely employed for efficient electrocatalytic reactions because they can provide a higher surface area with mesoporous structure, a good electrical conductivity, and so forth. The carbon-based support materials such as carbon black (CB) [16,17], carbon nanotubes (CNTs) [18], graphene (Gr) [19,20], and carbon nitride (C$_3$N$_4$) [21,22] are mostly used in catalytic processes. Recently, reduced graphene oxide (rGO) has attracted widespread interest for various applications due to its ultrahigh specific surface area and excellent chemical/mechanical/electrical properties [20].

In this study, we introduce an FeO$_6$-type hybrid cobalt framework, [Co$_7$(t-ca)$_{14}$(H$_2$O)$_2$] (t-ca = trans-cinnamate), as an efficient electrocatalyst and rGO as an electrochemical supporter for the OER. The electrocatalytic properties of the cobalt cinnamate(catalyst)/rGO composite were investigated using linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The electrocatalytic activity and stability of the catalyst/rGO composite were significantly improved compared to those of the catalyst alone.

2. Materials and Methods

2.1. Reagent

rGO (cat#805424), ruthenium(IV) oxide (RuO$_2$), iridium (IV) oxide (IrO$_2$), and Nafion solution (5% (w/w) in lower aliphatic alcohols/water mixture) were obtained from Aldrich. All chemicals were used as received. Ultrapure water (≥18 MΩ, Merck Millipore, Burlington, MA, USA) was used in all experiments.

2.2. Preparation of Electro catalyst

The catalyst, [Co$_7$(t-ca)$_{14}$(H$_2$O)$_2$], was prepared using a hydrothermal method previously reported [15]. Briefly, it was synthesized using a mixture of cobalt (II) chloride hexahydrate (9 M), trans-cinnamic acid (9 M), and 1,3-diaminopropane (3 M) in 1.0 mL of water, which was heated at 140 °C for 3 days. Violet polyhedral-shaped crystals were recovered by vacuum filtration. The full characterization of cobalt cinnamate including powder X-ray diffraction (XRD) analysis, thermogravimetric analysis, gas sorption property, and magnetic susceptibility are presented in a previous study [15].

The loading solutions of [Co$_7$(t-ca)$_{14}$(H$_2$O)$_2$] and rGO (the catalyst/rGO composite) and other control samples were prepared by dissolving 2 mg of catalyst, iridium(IV) oxide, or ruthenium(IV) oxide with/without 1 mg of rGO in 1 mL of water and ethanol (v/v 1:1) solution containing 20 µL of Nafion$^\text{®}$ p solution, respectively. Next, 2 µL of the prepared loading solution was dropped onto the cleaned glassy carbon electrode (GCE) (dia. 3 mm, ALS Co., Ltd., Tokyo, Japan) and dried for 0.5 h (Figure 1).
2.3. Electrochemical Characterization

Electrochemical measurements of linear sweep voltammetry (LSV) and rotating disk electrode (RDE) were taken using a CHI model 750d potentiostat (CH Instruments, Austin, TX, USA) and an RRDE-3A (ALS Co., Ltd., Tokyo, Japan). A conventional three-electrode cell, consisting of a sample-modified glassy carbon working electrode, an Ag/AgCl (Sat’d KCl, 0.198 V vs. NHE) reference electrode, and a Pt wire counter electrode were used in all electrochemical experiments. O₂-saturated 0.1 M KOH solution was used as an electrolyte for the OER experiments. The potentials for electrochemical measurement were reported vs. reversible hydrogen electrode (RHE) after 100% of IR compensation. The solution resistance obtained from the conductivity measurement was ~100 Ω. The potentials vs. RHE were calculated according to the following equation:

\[ \text{RHE} = E \ (\text{vs. Ag/AgCl}) + 0.059 \times \text{pH} + 0.198 \ V \]

For electrochemical impedance spectroscopy (EIS) measurement, an applied frequency from 0.001 Hz to 1000 kHz and signal amplitude of 5 mV were used. The O₂-saturated 0.1 M KOH electrolyte solution was used as an electrolyte.

3. Results

The electrocatalytic performance of the cobalt cinnamate(catalyst)/rGO composite was investigated for the OER. Figure 2a shows the linear sweep voltammograms (LSVs) of the catalyst/rGO composite-modified glassy carbon electrode (GCE) and bare/control/reference-material-modified GCEs for the OER at a scan rate of 5 mV/s using a rotating disk electrode (RDE).

The onset potential of the catalyst/rGO composite-modified GCE was less positive than the control and reference material-modified ones. The overpotentials (V₁) at a 10 mA cm⁻² of current density for the catalyst with/without rGO-modified GCEs were 327 and 358 mV, respectively (Table 1). The conventional electrocatalysts, RuO₂ with/without rGO and IrO₂ with/without rGO, have overpotentials of 560, 348, 370, and 385 mV, respectively. The overpotential of the catalyst/rGO composite was at least ~30 mV less than that of the control and reference materials.
Table 1. Overpotential, Tafel slope, and parameters corresponding to EIS response of electrocatalysts.

| Catalyst                        | $V_1$ (V at J = 10 mA cm$^{-2}$) | Tafel Slope (mV dec$^{-1}$) | $R_{cd}$ (Ω) | CPE (mF/cm$^2$) | $C_{dl}$ (mF/cm$^2$) |
|--------------------------------|---------------------------------|----------------------------|--------------|----------------|---------------------|
| catalyst/rGO                   | 327 mV                          | 27                         | 220          | 30             | 5.9                 |
| catalyst                       | 358 mV                          | 28                         | 630          | -              | 7                   |
| RuO$_2$/rGO                    | 560 mV                          | 127                        | -            | -              | -                   |
| RuO$_2$                        | 348 mV                          | 97                         | -            | -              | -                   |
| IrO$_2$/rGO                    | 370 mV                          | 103                        | -            | -              | -                   |
| IrO$_2$                        | 385 mV                          | 118                        | -            | -              | -                   |

1 Geometric area of the electrode used. 2 Double layer capacitance based on the non-Faraday charging current in CV.

The kinetic parameters were also investigated by Tafel plots (Figure 2b) [23]. The Tafel slopes of the catalyst/rGO composite- and catalyst-modified GCEs were 27 and 28 mV/dec, respectively (Table 1), indicating that the reference electrocatalysts, RuO$_2$ with/without rGO and IrO$_2$ with/without rGO, have Tafel slopes of 127, 97, 103, and 118 mV/dec, respectively.

Remarkably, these data suggest that the catalyst/rGO composite shows excellent electrocatalytic activity from both thermodynamic and kinetic perspectives towards the OER. It is superior to the catalyst alone or other noble metal oxide reference materials such as RuO$_2$ and IrO$_2$ with/without rGO supports.

Durability test is one of the most important factors for electrocatalysts. Therefore, long time chronoamperometry (CA) and multi-segment cyclic voltammetry (CV) experiments were conducted for the catalyst/rGO composite. The applied potential for the CA experiments were where the expected current densities were 10 mA cm$^{-2}$. The current density of the catalyst/rGO composite-modified GCE was maintained ≥70% for 12 h, which is a further improvement over that of the catalyst alone, ≥35%, as shown in Figure 3a. This result implies that the interaction between the catalyst and rGO is strong enough to maintain their anchoring during the vigorous gas evolution reactions such as OER.

The CV curves after 600 cycles were similar with the initial onset potential and current level, implying that the structural stability of the catalyst is retained after formation of the composite with rGO (Figure 3b).
Transportation of charge and ions are crucial factors in the higher electrochemical OER performance. Electrochemical impedance spectroscopy (EIS) was performed to investigate the electron transfer capacity associated with the electocatalytic properties. The Nyquist plots for the catalyst/rGO composite-modified GCE and the respective EIS parameters are presented in Figure 4 and Table 1, respectively. The charge transfer resistance ($R_{ct}$) values of the catalyst/rGO composite- and the catalyst-modified GCEs were 220 and 630 $\Omega$, respectively (Table 1). The constant phase element (CPE) of the catalyst/rGO composite-modified GCEs, 30 mF cm$^{-2}$, was also larger than that of the catalyst alone-modified GCE at 7 mF cm$^{-2}$. Similarly, the double layer capacitance ($C_{dl}$) values calculated from the non-Faraday charging current in CV measurement were 5.9 and 5.7 mF cm$^{-2}$, respectively. The small $R_{ct}$ and large CPE indicate the high electron transfer ability and large capacity of the 3D framework of the catalyst/rGO composite [24]. The small semicircle in the high-frequency domain appears to be the arbitrary effects by the instrument because typical electrochemical reactions are relatively slow and do not respond in the frequency domain above 100 kHz.

Figure 4. Nyquist plots of the catalyst-modified (black) and the catalyst/rGO composite-modified (red) GCEs recorded in O$_2$-saturated 0.1 M KOH electrolyte solution.

4. Discussion

Recently, many metal-organic frameworks (MOFs) have been developed due to their wide range of application [25,26]. Despite their versatility, such as porosity, catalytically active centers, and structural tunability, only a few catalysts have been reported because...
the organic part of MOF is relatively less stable compared to the metal-based nanomaterial catalysts. This is also the case with recently reported cobalt cinnamate, \([\text{Co}_7(l\text{-ca})_{14}(\text{H}_2\text{O})_2]\), which is highly active for OER but has weak durability [15]. The stability and durability of the electrocatalyst are important issues in industrial applications [17].

Therefore, in this study, we introduced rGO, which is a widely used carbon based support, to increase the stability and durability of the catalyst on the electrode surface. In particular, in many catalytic studies, graphene has been widely used as an excellent supporter due to its high electronic conductivity, large specific surface area, and outstanding stability [27–29]. In addition, Nafion, a conductive polymer, is also introduced as another additive to immobilize an electrocatalyst on the electrode and to reduce the resistance between the electrocatalyst and electrode [30].

As a result of the inclusion of the supporter, rGO, the onset potential and stability were improved, as shown in Figures 2 and 3. First, the reduced overpotential with rGO supports seems to be due to the strong interaction between the catalyst and rGO. Second, the improved durability may be caused by the increment of anchoring forces followed by the formation of higher density of the sample on the electrode surface.

The organic part, the \(\pi\)-conjugated cinnamate ligand, seems to play an important role in overpotential and durability improvements of composites. The cinnamate ion composed of styrene and carboxylate groups is likely to interact strongly with the rGO through \(\pi-\pi\) interactions and hydrogen bonds, respectively. Moreover, the \(\pi-\pi\) orbital delocalization of the catalyst by binding with rGO accelerates charge transfer followed by modulation of the electronic state of active center [31–33]. The strong interaction between the catalyst and supporter is confirmed by the significant reduction in charge transfer resistance in EIS measurement (Figure 4). Therefore, this result suggests that hybridization of the catalyst with the rGO can manage the electrocatalytic activity of the composite toward OER [34], and in this case it works well.

Meanwhile, the catalytic activities of \(\text{RuO}_2/r\text{GO}\) and \(\text{IrO}_2/r\text{GO}\) composites are worse than \(\text{RuO}_2\) or \(\text{IrO}_2\) because these catalysts have no organic part to interact strongly with the supporter, rGO; on the contrary, mixing of rGO seems to interfere with the electric conductivity of \(\text{RuO}_2\) or \(\text{IrO}_2\) and the mass transfer of reagent, resulting in a large overpotential and slow kinetics, respectively.

The strong anchoring force by using rGO improves the adhesiveness, stability, and durability of the catalyst on the electrode surface. The strong adhesion of catalyst with supporter can be observed by the scanning electron microscopy (SEM) of catalyst distributed electrodes. As shown in Figure 5, the morphology of the catalyst/rGO composite-modified electrode was rougher than the catalyst-modified one, indicating that the amount of attached catalyst was much greater than without supporter, which is confirmed by the energy dispersive spectroscopy (EDS) quantitative analysis. The larger amount of catalyst on the rGO supported electrode is also identified by the increased CPE value in EIS measurement.

Transmission electron microscope (TEM) characterization was also carried out to show the microstructure or morphology of the catalyst/rGO composite. (Figure S1 in Supplementary Material). However, it was difficult to observe the distinguishable boundary between the catalyst and the supporter because both the catalyst and supporter are organic. However, EDS quantitative analysis shows the distribution of Co atoms over the composite.

X-ray photoelectron spectroscopy (XPS) analysis was performed to obtain information about the electronic structure modulation of the catalyst/supporter composite. Figure 6 shows the XPS spectra for C, O, and Co of the catalyst and the catalyst/rGO composite after OER.
Figure 5. SEM and EDS analyses of (a) the catalyst/rGO composite-modified and (b) catalyst-modified GCEs. The red color in the bottom images is the element mapping for C.

The main C 1s peaks were obtained at 291.5 eV (purple line) in the catalyst and 284.5 eV (red line) in the composite. The peaks at 291.5 and 284.5 eV represent the C connected to the highly electronegative atoms (e.g., CO$_3^{2-}$ or CF$_2$) and C in highly oriented pyrolytic graphite (HOPG), respectively [35]. Therefore, the increment of the peak size (counts) in the whole binding energy region and the shift of main peak from 291.5 to 284.5 eV indicate the successive introduction of rGO into the catalyst.

In Figure 6b, the O 1s peaks at 529.4 (blue line) and 531.1 eV (red line) represent the lattice oxygen and oxygen vacancy (defect), respectively, consistent with the literature [36,37]. For the catalyst, the strongest peak at 531.1 eV, corresponding to the oxygen vacancy, was still retained after the composite formation. Notably, the larger area of the peak at 531.1 eV of the composite than the catalyst alone implies more oxygen vacancies and a higher electrocatalytic activity of the composite [36].

In Figure 6c, for catalyst, the Co 2p peaks at ~778.6 and ~793.6 eV with small satellite peaks were observed. For the composite, the Co 2p peaks appear at a lower binding energy region, ~777.5 and ~792.5 eV, which reveals the electronic interaction between the catalyst and rGO [38].
Figure 6. XPS spectra for (a) C 1s, (b) O 1s, and (c) Co 2p regions using the catalyst alone or the catalyst/rGO composite-modified indium tin oxide electrode after electrochemical measurements.

5. Conclusions

We demonstrated the electrocatalytic activity of an I 3O0-type inorganic hybrid electrocatalyst, cobalt cinnamate, supported on rGO for the OER. Even with a supporter, the fast mass and charge transport in the 3D inorganic network and a proper electronic structure modulation of the active center by effective electron conjugation of the catalyst is conferred to the catalyst/rGO composite. The hybrid electrocatalyst/supporter composite
5. Conclusions

We demonstrated the electrocatalytic activity of an $\Gamma^3\mathrm{O}^0$-type inorganic hybrid electrocatalyst, cobalt cinnamate, supported on rGO for the OER. Even with a supporter, the fast mass and charge transport in the 3D inorganic network and a proper electronic structure modulation of the active center by effective electron conjugation of the catalyst is conferred to the catalyst/rGO composite. The hybrid electrocatalyst/supporter composite formed by strong interactions between the organic part of the catalyst and graphene exhibits fast kinetics, reduced overpotential, and improved durability. The overpotential of the catalyst/rGO composite was 327 mV, which is 31 mV less than the catalyst alone. The stability and durability of the electrocatalyst were improved due to the strong anchoring force between the catalyst and rGO. The electrocatalytic current level of the catalyst/rGO composite was retained at $\geq$70% after a reaction time of 12 h, compared to $\geq$35% for the catalyst alone. Overall, the rGO supporter played an important role in the OER performance of cobalt cinnamate catalyst. The improvement of electrocatalytic properties of the composite is due to the feasible chemical interactions between rGO and $\pi$-conjugated hydrocarbon/carboxylate groups of the cinnamate ligand. An appropriate combination of catalyst and supporter components to enhance the electrocatalytic properties of the composite provide a new direction in the application of MOF electrocatalysis. The epitaxial growth of the cobalt cinnamate using rGO under hydrothermal conditions could be a subject worth looking into in future research to increase the interaction between catalyst and supporter.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en14165020/s1, Figure S1: Transmission electron microscope (TEM) and energy dispersive spectroscopy (EDS) image of the cobalt cinnamate/rGO composite after electrochemical measurement, Figure S2: TEM image of the cobalt cinnamate after electrochemical measurement, Figure S3: The equivalent circuit for the calculation of EIS parameters, Figure S4: XPS spectra for (a) C 1s, (b) O 1s, and (c) Co 2p regions using the catalyst/rGO composite-modified indium tin oxide electrode before and after electrochemical measurements.

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