Carbon-Supported IrCoO\textsubscript{x} nanoparticles as an efficient and stable OER electrocatalyst for practicable CO\textsubscript{2} electrolysis

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ABSTRACT

The development of an efficient and stable oxygen evolution reaction (OER) electrocatalyst operating under pH-neutral conditions is vital for the realization of sustainable CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR) systems in the future. For commercializing this system, it is also important to be able to use general-purpose water as an electrolyte. Here, we explore, characterize and validate a new IrCoO\textsubscript{x} mixed metal oxide as an efficient and stable OER catalyst, before we investigate and proof its suitability as counter electrode to a CO\textsubscript{2}RR cathode operating under pH-neutral conditions. More specifically, carbon-supported IrCoO\textsubscript{x} core-shell nanoparticles exhibited a highly efficient OER catalytic activity and stability compared to state-of-art reference IrO\textsubscript{x} catalysts in CO\textsubscript{2}-saturated 0.5 M KHCO\textsubscript{3} tap-water. IrCoO\textsubscript{x}/C also exhibited a significantly improved electrochemical oxidation and corrosion resistance than IrO\textsubscript{x}, resulting in a beneficial suppression of Ir dissolution. The application of IrCoO\textsubscript{x}/C in the CO\textsubscript{2} electrolyzer displayed superior CO space-time yields over prolonged electrolyzer tests.

1. Introduction

The electrochemical conversion of CO\textsubscript{2} to high energy density fuels and valuable chemicals is generally considered a sustainable method for reducing CO\textsubscript{2} emissions and storing intermittent renewable electricity.\textsuperscript{[1–3]} The overall CO\textsubscript{2} electrolysis process is typically divided into two half-cell redox reaction: CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR) and oxygen evolution reaction (OER).\textsuperscript{[4,5]} Typically, a CO\textsubscript{2}RR is carried out in neutral or marginally alkaline solutions because of the low solubility of CO\textsubscript{2} in alkaline media and the competitive formation of hydrogen in acidic media.\textsuperscript{[6]} In this regard, an OER in near-neutral pH electrolytic media is also crucial for the development of CO\textsubscript{2}RR devices. However, OER requires large overpotentials owing to the slow kinetics of the multiple proton-coupled electron transfer.\textsuperscript{[7]} In addition, an OER activity under near-neutral pH conditions exhibits a relatively low efficiency owing to the low ionic conductivity caused by the low concentration of deprotonated water molecules.\textsuperscript{[8]} Therefore, several studies have been focused on identifying efficient electrocatalysts for an OER in a neutral electrolyte, such as precious metal oxide\textsuperscript{[9]}, transition metal oxide\textsuperscript{[10]}, perovskite\textsuperscript{[11]}, phosphate\textsuperscript{[12]}, chalcogenides\textsuperscript{[13]}, and molecular catalyst\textsuperscript{[14]}. Among these, the IrO\textsubscript{x}-based electrocatalyst has been universally accepted as the state-of-the-art OER catalyst. It maintains a stable structure during water oxidation over a broad pH range\textsuperscript{[15–17]}. However, Ir has the problems of high cost and scarcity as a precious metal, which severely hinders its widespread application.\textsuperscript{[18,19]} In order to overcome these issues, many studies have focused on reducing the electrocatalyst loading without sacrificing on the catalytic performance.

An effective approach is to use a high-surface-area support material. This can increase the dispersion of catalyst nanoparticles and increase
the active surface area, thereby increasing the utilization of the electrocatalyst [20,21]. In general, carbon materials are used to support electrocatalysts by providing an electrical pathway and to stabilize nanoparticles without agglomeration [22–25]. However, a highly corrosive environment (such as one where a high potential is applied for an OER under an acidic or alkaline condition) accelerates electrochemical carbon corrosion. Electrochemical carbon corrosion has been regarded as a cause of degradation of catalytic activity owing to the migration, aggregation, and detachment of nanoparticles [26,27]. Therefore, graphitized carbon [28], metal carbide [29], metal nitride [30], and conductive metal oxide [31], have received much attention as corrosion-resistant support materials in electrocatalyst systems. Xing et al. prepared IrOx@Ir nanoparticles supported on TiN for oxygen evolution in acidic media, which is more active and stable than unsupported IrO2 [30]. They explained that TiN is used to downshift the d-band center of Ir in IrOx@Ir/TiN compared to pure IrO2 resulting in the improved OER catalytic activity and stability. We also observed that an antimony-doped tin oxide (ATO) support mitigates Ir3+ dissolution in the electrolyte and suppresses the Ir oxidation during water splitting [32]. This result substantiated the catalyst-support interaction, which stabilized the IrOx nanoparticles on ATO with the sustained lower Ir oxidation states. Although these materials exhibit improved electrochemical corrosion resistance in an OER environment, some problems have been pointed out such as corrosion of dopants, [33] deterioration of electrical conductivity [34], and low surface area [35].

Another approach is to prepare nanosized Ir alloy metal oxide using inexpensive metals. This can improve the OER performance and reduce the use of Ir electrocatalyst [36–40]. We previously reported that dealloyed IrNi@IrOx core-shell nanoparticles exhibit remarkable OER activity up to three-fold improvement compared to IrO2 electrocatalyst [41,42]. The concept of core-shell nanoparticle represents an effective strategy to maximize the utilization of precious metals. Lowering the energy of Ir 5d-orbitals below those of O 2p orbitals (inverted band situation) in highly lattice-defective IrNi@IrOx catalysts resulted in strongly improved intrinsic and mass-based OER catalytic activity, which aids in reducing the effective Ir catalyst mass loading. [42] Huang and co-workers developed monodispersed IrM (M = Ni, Co, and Fe) nanocatalysts through a surfactant-free method [43]. The prepared Ir-based electrocatalysts has a small particle size and clean surface. They exhibit performance higher than that of Ir nanoparticles for OER under acidic electrolyte and reduce the usage of expensive noble metals. Yang et al. synthesized Cu0.5Ir0.5O2 for OER and its improved activity was explained in terms of the d-orbital occupation states of the Ir 5d orbital in IrO2 [44]. The doped Cu metal alters the Ir electronic structure and lifts its εf orbital resulting in partial occupation of its d2 orbital. Although Ir metal has been widely used to OER electrocatalysts, the activity and durability of Ir alloy electrocatalyst in neutral electrolyte for CO2RR system has received only negligible attention to date.

In this study, we report catalytically highly active carbon-supported IrCoOx OER nanoparticles operating in pH neutral conditions. Co was used as the dopant metal of Ir, owing to its high OER activity in a neutral electrolyte. Carbon black was possible to use as a catalyst support because its electrochemical oxidation in pH neutral media is kinetically much slower than that in other media. [45] The synthesized IrCoOx/C catalyst exhibited much higher catalytic efficiency compared to IrO2/C at neutral pH. The molecular origin of the favorable catalytic behavior was clarified using in situ/operando X-ray Absorption Spectroscopy (XAS). For analyzing OER electrocatalysts in practical CO2RR systems, tap water was used as an electrolyte media. Moreover, the long-term durability test of the OER was conducted in CO2-saturated 0.5 M KHCO3 for 216 h. After the stability test, the XPS, in situ/operando ICP-MS, and HR-TEM results demonstrated that IrCoOx/C exhibits higher corrosion-resistance than that of IrO2/C. To verify the feasibility of OER electrocatalysts in a CO2RR system, the synthesized IrCoOx/C was applied to CO2 electrolyzer, which showed higher CO partial current density compared with IrO2/C at identical cell potential region. Based on these results, we could evaluate the applicability of IrCoOx and the carbon support in an OER in realistic-neutral water media.

2. Experimental section

2.1. Preparation of Ir–Co alloy nanoparticles supported on carbon

IrCo alloy nanoparticles were synthesized by applying previously reported methods. [41] Co (II) tetrahydrate (≥ 98.0 %, Sigma Aldrich), carbon black (acetylene, 50 % compressed, Alfa Aesar), 0.66 mmol of 1,2-tetradecanediol (90 %, Sigma Aldrich), oleyamine (70 %, Sigma Aldrich), and 0.45 mL oleic acid (99 %, Alfa Aesar) were dissolved in 45 mL of dibenzyl ether (99 %, Alfa Aesar). The mixture solution was heated to 80 °C for 30 min in a N2 atmosphere. The temperature was increased to 240 °C. Then, Ir(ac)3 (Chempur, 48 wt% Ir) was added to the mixture. The reaction solution was refluxed at 240 °C for 1 h and then cooled down to room temperature. 60 mL of ethanol (Sigma Aldrich) and 30 mL of toluene (Sigma Aldrich) were added to the resulting suspension. This was followed by sonication for 10 min. The stirring was continued for an additional 3 h. In order to remove excess surfactant and solvent, the final product was centrifuged and washed with ethanol five times (8200 rpm, 30 min). The powder produced was dried in a freeze dryer for 24 h and then calcinated at 180 °C in air for 2 h. This was followed by purging with N2 gas for 2 h at 300 °C.

2.2. Physical characterizations

The morphology of the fabricated catalyst was measured by high-resolution transmission electron microscopy (HR-TEM) using a FEI Titan 80-300. Powder X-ray diffraction (XRD) patterns were obtained using an Empyrean (Malvern PANalytical) equipped with Cu K-alpha radiation. Identical location transition electron microscopy (IL-TEM) was used to investigate the same nanoparticle prior to and after the electrochemical treatment. The prepared electrocatalysts were deposited on a gold-finder grid coated with carbon film (Agar Scientific) and used as the operating electrode in a typical three-electrode system. X-ray photoelectron spectroscopy (XPS) was performed using a K-alpha radiation (Thermo Scientific) with monochromatic X-rays generated by an Al K-alpha source. The content of the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-AES; iCAP 7000, Thermo Scientific). In situ/operando X-ray absorption spectroscopy (XAS) was performed with an electrochemical flow cell at the 1D KIST-PAL beam line of Pohang Accelerator Laboratory, Pohang, South Korea. The 1D beam line has a Si (111) double crystal monochromator for a photon energy range of 4–16 keV. The program Athena was used for identifying the absorption edge and to normalize the EXAFS profiles through pre-edge and post-edge background subtraction from raw absorption data. In situ/operando ICP-MS coupled with a homemade electrochemical flow cell was used to quantitatively measure the dissolution behavior of Ir-based OER electrocatalysts. The relevant details of in situ/operando measurements are described in Supporting Information (SI).

2.3. Electrochemical characterizations

The electrochemical properties of the Ir-based electrocatalysts were investigated using a rotating disk electrode (RDE, Pine Research instrument) and VSP Potentiostat (Bio-Logic Science Instruments). The experiment was performed in a three-electrode system in a CO2-saturated 0.5 M KHCO3 (99.7 %, Sigma-Aldrich) aqueous solution (pH 7.4). The solution was prepared using common tap water (sourced from the service in Seoul, Korea). A glassy carbon electrode (Fixed-disk RDE tip, 0.196 cm2) with a thin film of the prepared sample was used as a working electrode. A saturated Ag/AgCl (3.5 M KCl) and a platinum
wire as a reference and counter electrode, respectively. The catalyst inks were prepared by dispersing the 5 mg of catalysts in 5 mL solvent (2.49 mL of DI water, 2.49 mL of isopropanol, and 20 μL of 5 wt% Nafion solution). After the sonication of the suspension for 20 min using ultrasonic homogenizer process (Bandelin), the resulting solution was dropped onto the glassy carbon electrode. The total metal loading of iridium was fixed to 3 μg cm⁻². Prior to electrochemical measurement, cyclic voltammogram (CV) was conducted to oxidize iridium based electrocatalysts in 0.05 M H₂SO₄ between 0.05–1.5 V vs. RHE at a 500 mV s⁻¹ scan rate for 50 cycles. The OER polarization curve was measured at a 10 mV s⁻¹ scan rate and a 1600 rpm rotation speed in CO₂-saturated 0.5 M KHCO₃ tap water. For the long-term stability test, the catalyst was loaded on the gold coated titanium foil (1.0 mm thick, 99.2 %, Alfa Aesar) using a spray-coating technique. The total iridium loading was 0.5 mg cm⁻² and the electrode area was 0.196 cm². The stability test was carried out at 5 mA cm⁻² for 9 days (216 h). In order to evaluate the durability of IrCoOₓ for OER under practical conditions, stability test was performed for 20 h at 100 mA cm⁻² in single cell water electrolyzer. The synthesized IrCoOₓ/C and commercial Pt/C catalyst (TANAKA) were sprayed on carbon paper (SIGACET® GDL, SGL Group) as the anode and cathode, respectively. The single cell structure is described in Figure S14. CO₂ saturated 0.5 M KHCO₃ tap-water electrolyte was fed to the anode and cathode for a CO₂ electrolysis environment.

2.4. CO₂ electrolysis operation and product analysis

The gas-fed electrochemical flow cell was used to carry out the electrochemical CO₂ reduction reaction. The synthesized IrCoOₓ/C and commercial Ag nanoparticle (AgNP, Alfa Aesar) were deposited on carbon paper (SIGACET® GDL, SGL Group) as the anode and cathode, respectively, by using a spray coating method. The geometric area of each of the electrodes was 10 cm². An anion exchange membrane (Sustainon® X37-50, Dioxide Materials™) was used to separate the each of the electrodes was 10 cm². An anion exchange membrane (Sustainon® X37-50, Dioxide Materials™) was used to separate the gas/electrolyte. The first and 50th activation the CV of IrCo/C in Figure S4 – S6 show the IL-TEM images of IrCo/C before and after the electrochemical oxidation process. We can confirm that the surface of IrCo with aligned metallic structure converted to amorphous IrCoOₓ surface with the leaching of Co. In order to confirm the change of Co ratio, EDS of Co was measured before and after electrochemical oxidation. As shown in Figure S7, Co ratio of IrCo/C was significantly decreased from 26.4 % to 9.5 % after the oxidation process.

To apply IrCoOₓ/C activated in an acidic condition to the CO₂RR system, the OER activity was measured under neutral condition. Linear sweep voltammetry (LSV) were measured in CO₂-saturated 0.5 M KHCO₃ solution at a scan rate of 10 mV s⁻¹ and a rotating speed of 1600 rpm. Figure 2 shows that the IrCoOₓ/C catalyst exhibits higher OER catalytic activity than IrOₓ/C catalyst with smaller particle size. To evaluate the OER catalytic kinetics in the neutral condition, Tafel plots and Ir mass-based activity of all samples were calculated from LSV curves, and the results are shown in Figure 2c. At an overpotential of 280 mV, the mass activity of IrCoOₓ/C is 146 A g⁻¹, which is significantly higher than that of IrOₓ/C (111 A g⁻¹). In general, the Tafel-slope is an important kinetic parameter to reveal changes in the apparent OER mechanism. IrCoOₓ/C displays a Tafel slope of 105 mV dec⁻¹, which is smaller than that of IrOₓ/C (133 mV dec⁻¹), suggesting that IrCoOₓ/C has high reaction kinetics for OER. In previous research, IrNix@IrOₓ catalyst exhibit enhanced performance than Ir catalyst. Despite of small ratio of Co component, remarkable OER activity of IrCoOₓ/C is derived from alloy effect. Furthermore, the dissolution of Co on the surface of IrCo nanoparticles can change the electronic structure of the catalyst, which increases the OER catalytic activity [42].

3.3. Electronic structure of IrCoOₓ catalyst in neutral condition

To investigate the correlation between the OER catalytic activity and an electronic structure under a neutral condition, we measured the in situ/operando X-ray absorption fine structure (XAFS) of IrCoOₓ/C.
Fig. 1. (a) Low- and (b) high-resolution TEM images of the synthesized IrCo alloy nanoparticles supported on carbon. (c-e) HAADF-STEM elemental mapping analysis of IrCo/C. Red, green, and blue represent Ir, Co, and carbon, respectively. (f) EELS line-scan profiles of IrCo alloy nanoparticle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

prepared in a CO₂-saturated 0.5 M KHCO₃ solution. Fig. 3a shows the Ir L₃-edge X-ray absorption near-edge spectroscopy (XANES) region of the IrCoOₓ/C and IrOₓ/C at different values of applied potential. For comparison, commercial Ir compounds (Ir foil, IrCl₃, and IrO₂) were also measured as references, under a similar condition. The sharp peak in Fig. 3a is called the white-line which is generated by the electronic transition from a 2p orbital to a vacant 5d orbital states. [48–50] A shift of the white-line toward higher energies typically implies an increase in the number of d-band holes and oxidation state. Therefore, the higher-energy peak position of IrCoOₓ/C under a catalytic OER condition at 1.5 V_RHE indicates that IrCoOₓ/C has a higher Ir oxidation state and more d-band holes than IrOₓ/C does. Fig. 3b shows a fit of the white line energy as a function of the formal d-band hole count of the catalysts and reference materials. This type of plot aids in quantitatively elucidating the shift of the white lines. The increase by 0.965 eV per d-band hole was calibrated based on the Ir foil (5d⁶ 6s², Ir), IrCl₃ (5d⁶ 6s³, Ir³⁺), and IrO₂ (5d⁶ 6s¹, Ir⁴⁺) standards. The measured peak positions were fitted in the calibration curve. The calculated d-band hole numbers of IrCoOₓ/C and IrOₓ/C at 0.4 V_RHE is between those of Ir foil (3.0) and IrCl₃ (4.0). Under catalytic OER conditions at 1.5 V_RHE, the formal d-band hole counts of IrCoOₓ/C and IrOₓ/C were 5.8 and 5.2, respectively. This indicates that IrCoOₓ/C has a higher oxidation state than IrOₓ/C does. This can be explained by the leached Co in the electrochemical oxidation step, which generates the lattice vacancies on the surface of IrCoOₓ to increase the number of d-band holes and oxidation states of Ir. [42] These results support our initial conjecture of improved OER catalytic activity of IrCoOₓ/C in the neutral condition (Fig. 2b) and gives a molecular explanation for it. We also measured the extended X-ray absorption fine structure (EXAFS) of the electrocatalysts to study the change of the local geometric structure under neutral OER condition. Fig. 3c shows the Fourier transforms of IrCoOₓ/C and IrOₓ/C with different applied potentials under CO₂-saturated 0.5 M KHCO₃. In general, the EXAFS result depends on the characteristic interference pattern between the outgoing photoelectrons from the absorption center and the backscattered photoelectrons from adjacent atoms, indicating the identity of the surrounding atoms as well as their coordination geometry and degree of disorder. [51] The peak of IrOₓ/C at the reduced distance of approximately R = 2.5 Å is associated with the radial distance of the metallic Ir–Ir bond. It decreased significantly at 1.5 V_RHE. This change confirmed that metallic Ir of IrOₓ/C was oxidized under OER conditions (+ 1.5 V_RHE) under the neutral condition close to completion. IrCoOₓ showed a shorter reduced distance of the metal-
metal bond (Ir–Ir and Ir–Co) compared to IrOx/C, which is due to the alloying effect of Ir and Co. The presence of Co in the Ir lattice caused the X-ray back scattering property to change, which significantly altered the EXAFS spectrum. It is noteworthy that IrCoOx/C maintains the peak of the metal–metal bond even at 1.5 V_RHE under neutral conditions. This indicates that metallic IrCo remained to be present in the core of the nanoparticles and that the electrochemically oxidized IrCoOx is concentrated in the shell. The peaks at approximately R = 1.5 Å represents the radial distance of the Ir–O bond. For the IrCoOx/C at 1.5 V_RHE, the peak position of the Ir–O radial distance was shorter than that of IrOx/C. The shortened Ir–O metal–ligand distance of IrCoOx/C reflected the presence of lattice-defects in the Co depleted near surface region of the catalyst particles. Cationic lattice defects, in turn, are known to induce the formation of electrophilic oxygen ligands (ligand holes), which readily form O=O bonds with nucleophiles resulting in a higher OER catalytic activity. [42]

3.4. Electrochemical stability of IrCoOx catalyst in neutral tap water condition

To investigate the practical feasibility of IrCoOx/C as an anode electrocatalyst in combination with a CO2RR cathode in a CO2 electrolyzer system, we measured its long-term durability at constant current density of 5 mA cm⁻² for 216 h (9 days) in CO₂-saturated KHCO₃ tap water, which is representative of general water, was used as the electrolyte media for a realistic implementation of the system. For comparison, IrOx/C was also measured under an identical condition. As shown in Fig. 4a, the initial potential of IrOx/C is lower than that of IrCoOx/C owing to high OER catalytic activity of IrCoOx/C. The measured electrode potential of IrOx/C was stable until 25 h and gradually increased up to 110 h. Then, the overpotential for 5 mA cm⁻² increased exponentially, which is attributed to the decrease in the electrochemically active surface area (ECSA) of IrOx. In contrast, IrCoOx/C exhibited only an overpotential increase of 150 mV during the 216 h. The electrochemical stability of IrCoOx/C was once more confirmed in water electrolysis cell at the constant current density of 100 mA cm⁻² for more practical application (Fig S10). These verified that IrCoOx and carbon black support exhibits high electrochemical stability for OER in tap water-based neutral condition. In order to quantify the stability of IrOx and IrCoOx nanoparticles, in situ/operando ICP-MS was carried out. The results are shown in Fig. 4b. The stability test for in situ/operando ICP-MS was carried out by cyclic voltammetry and chronoamperometry techniques. This is clearly shown in the top of Fig. 4b. The Ir dissolution profiles of IrOx/C and IrCoOx/C in the neutral condition are proportional to the applied potential, but the resolution of the peaks is not clear due to the neutral condition reaction and slats in the electrolyte. The Ir dissolution rate of IrCoOx/C is slower than that of IrOx/C indicating IrCoOx/C is more stable, and these results are in good agreement with the results of chronopotentiometry stability test. Interestingly, IrOx/C has a low current density at 1.85 V_RHE but high Ir dissolution concentration, which implies that the oxidation current of IrOx is used for Ir dissolution rather than oxygen evolution. These results indicate that IrCoOx/C is electrochemically stable and suppresses Ir dissolution compared to IrOx/C, which implies that IrCoOx nanoparticles and carbon support are suitable as anode electrocatalysts for CO2RR system with tap water based neutral condition.

3.5. Physical properties of IrCoOx catalyst prior to and after stability test in neutral tap water condition

To further understand the enhanced stability of IrCoOx/C, we performed X-ray photoelectron spectroscopy (XPS) on the IrOx/C and IrCoOx/C electrocatalysts before and after the stability test. The measured Ir 4f spectra are shown in Fig. 5a and b. The Ir spectrum can be deconvoluted into two peaks corresponding to Ir⁴⁺ and Ir⁴⁺, which are represented by the green and pink curves, respectively. The Ir⁴⁺/Ir⁴⁺ ratio of IrOx/C before stability test is 51.1 %, which is close to 48.9 % of IrCoOx/C. However, after stability test, the Ir spectrum of IrCoOx/C exhibits positively shifted peak position compared to that of IrOx/C. The Ir⁴⁺/Ir⁴⁺ ratio of IrOx/C is found to be 64.1 %, which is larger than the value of IrCoOx/C (54.0 %). It is noteworthy that the ratio of metallic Ir in IrCoOx/C was almost maintained even when the stability test was carried out in the OER operating condition. In situ/operando XAS and XPS results indicate that the electrochemically oxidized IrCoOx/C possesses amorphous IrCoOx layer with high d-band hole and maintains the metallic state of IrCo in the core under the OER condition, improving
Fig. 3. In situ/operando X-ray absorption spectroscopy (XAS) results of IrCoO$_x$/C at different applied potentials under CO$_2$-saturated 0.5 M KHCO$_3$. The setup is shown in Figure S8. For comparison, IrO$_x$ supported on carbon was measured under a similar condition. (a) Ir L$_\text{III}$-edge XANES region of IrCoO$_x$/C and IrO$_x$/C. XANES of Ir foil, IrCl$_3$, and IrO$_2$ are shown in (a) as references. (b) White-line position of IrCoO$_x$/C (circles) and IrO$_x$/C (squares) as a function of formal d-band hole count. (c) $k^3$-weighted Fourier transforms of EXAFS profiles collected at Ir L$_\text{III}$-edge of IrCoO$_x$/C and IrO$_x$/C at different applied potentials. Vertical blue solid lines indicate the Ir–O and Ir–Ir reduced distances of IrO$_2$ and Ir-foil, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. (a) Chronopotentiometry stability test of IrCoO$_x$/C electrocatalysts for OER in comparison to IrO$_x$/C catalyst under identical conditions. Measurement conditions: 25°C, CO$_2$-saturated 0.5 M KHCO$_3$ tap water, 5 mA cm$^{-2}$. Test time: 216 h. Ir loading: 20 µg cm$^{-2}$. (b) In situ/operando ICP-MS results of IrO$_x$/C and IrCoO$_x$/C in CO$_2$-saturated 0.5 M KHCO$_3$ tap water during cyclic voltammetry (CV) from 0.95 to 1.85 V RHE and chronoamperometry at 1.85 V RHE. The setup of in situ/operando ICP-MS is shown in detail in Figure S9.

catalytic activity and long-term stability compared to IrOx/C in the neutral electrolyte condition. Similar results have been reported in previous studies also; moreover, they explained that the alloy or core-shell structure of electrocatalysts improves the long-term stability by altering the electronic structure of the electrocatalysts. [52,53] For the C1s spectra of the electrocatalysts after the stability test (Fig. 5c), the carbon peak is decomposed into four components corresponding to sp2C (284.0 eV), sp3C (285.0 eV), C=O (286.2 eV), and CO (288 eV). In general, the peaks of the oxidized forms of carbon such as C=O and CO represent carbon corrosion [52]. The oxygen-associated peaks of IrOx/C are higher than those of IrCoOx/C. This implies that IrOx/C is more corrosive than IrCoOx/C because IrOx/C is unstable and over-potential is increased during the stability test.

TEM characterization was performed before and after stability test to obtain direct visual changes of electrocatalyst morphology. Fig. 5d and S11 show that the nanoparticles of IrOx/C were observed to grow and highly aggregate on the carbon black support due to the well-known phenomena of Ostwald ripening. [54] These results provide the evidence for the devastating morphology changes of IrOx/C after stability test, which reveals a direct influence on the catalyst performance decay. Meanwhile, IrCoOx nanoparticles agglomerate less compared to IrOx/C nanoparticles. Moreover, the structure of the carbon nano-particle is maintained, as shown in Fig. 5e and S12. These are in good accord with the results of chronopotentiometry, in situ/operando ICP-MS, and XPS. To quantify the element ratio of IrCoOx/C after stability, we carried out the TEM EDS analysis after stability test. As shown in Figure S13, the ratio of Ir (95.2 %) and Co (4.8 %) is closed to that before stability test. Based on these results, it is speculated that IrCoOx/C is more durable during OER in the neutral condition than IrOx/C due to the change of electronic structure and enhanced OER catalytic activity.

3.6. CO2RR performance with IrCoOx catalyst in the large scale electrolyzer

The new IrCoOx/C was deployed as anode OER electrocatalyst in a single cell, large active area-scale CO2 electrolyzer for the production of CO streams. To overcome the low performance and CO2 solubility problems in aqueous-phase CO2RR, we used the CO2 gas-feeding electrolysis system, as shown in Fig. 6a [55]. Humidified CO2 gas as catholyte and CO2-saturated 0.5 M KHCO3 tap water as anolyte were fed to the cathode and anode, respectively. The produced gases were analyzed and quantified using gas chromatography. A more detailed description is provided in Figure S14. Fig. 6b shows an electrochemical flow cell for CO2RR based on a water electrolysis device and the reference electrode was inserted into the flow field of the anode to measure the potential applied to each electrode. Commercial Ag nanoparticle
deposited on carbon paper was used as a cathode for reducing CO₂ to CO. IrCoOₓ/C was coated on Ti foam and used as an anode for the OER. For comparison, IrOₓ/C was also prepared under the similar condition. Fig. 6c shows the performance characteristics of the CO₂ electrolyzer with different OER electrocatalysts in the anode. The CO₂ electrolyzer was operated in chronoamperometry mode, in which the individual current density was measured when the cell was operated with different potentials from OCV to 3 V. The potential applied to the anode was measured through the reference electrode and cathode potential was calculated by subtracting the anode potential from the total cell potential. From the polarization curves for CO₂RR in the single cell condition, the membrane electrode assembly (MEA) with IrCoOₓ/C exhibited 181 mA cm⁻² at a cell voltage of 3 V, which is about twice as high as the MEA containing IrOₓ/C (94 mA cm⁻² at 3 V). The two cathode curves overlap almost completely because the same commercial AgNP was used as the electrocatalyst for CO₂RR. For the anode curve, the overpotential of IrCoOₓ/C was lower than that of IrOₓ/C under the similar current OER condition. Fig. 6d shows the CO Faradaic efficiency and partial current density for CO production on different OER electrocatalyst at various potential in single cell condition. All the data are recorded at scan rate of 10 mV s⁻¹ without iR-compensation. The Ir and Ag NP loading amount on anode and cathode are 0.5 and 1.0 mg cm⁻², respectively.

Furthermore, the improved OER activity of IrCoOₓ/C in CO₂ electrolyzer can improve the energy efficiency by obtaining a high current density at the same cell potential.

4. Conclusions

We have explored a new carbon-supported IrCoOₓ OER electrocatalyst for deployment and operation inside an anode layer used as counter electrode to a CO₂RR cathode inside a single cell CO₂ electrolyzer. The new IrCoOₓ/C exhibited a clearly higher OER catalytic activity than a reference IrOₓ/C catalyst, which was analyzed on the molecular scale using in situ/operando X-ray absorption spectroscopy (XAS) techniques and analyses. The Co depleted IrCoOₓ/C catalyst, in which the surface Co of IrCo nanoparticles leached in the acidic electrolyte, displayed a larger d-hole character and reduced Ir-O distance between the Ir centers and their O ligands under OER operating conditions. The experimentally observed, clearly shorter Ir-O distance and the associated changes in the electronic band structure of IrCoOₓ/C (lowering of Ir 5d states, while lifting of O 2p state) that favor the formation of oxygen ligand holes with reduced kinetic barriers toward O–O bond formation by nucleophilic attack is proposed to be the mechanistic origin for the favorable OER activity. In the long-term durability test, the IrCoOₓ/C exhibited stable OER performance for 216 h in metal-ion rich tap water-based neutral condition when compared to IrOₓ/C. This result was confirmed by in situ/operando ICP-MS and XPS, and it was found that Ir dissolution was suppressed because the metallic-Ir of core in IrCoOₓ/C has remained during neutral OER. Furthermore, the IrCoOₓ/C confirmed their RDE-based OER catalytic
activity in realistic CO₂ electrolyzer testing. The CO₂ RR system with IrCoOₓ/C applied to the anode showed a CO partial current density of 181 mA·cm⁻² and a CO Faradic efficiency of 100% at a cell potential of 3 V. These results demonstrate that IrCoOₓ/C has high OER catalytic activity under tap water based neutral electrolyte condition and that carbon support is stable in the neutral OER environment, unlike acidic or alkaline condition. Our observations may provide insights into the synthesis of OER electrocatalysts with improved durability and activity under realistic neutral conditions.

Author contributions

W. H. Lee designed/conducted the experiments, analyzed the data and wrote the manuscript. H. N. Nong contributed to the synthesis of the electrocatalysts. C. H. Choi contributed to the analysis of in-situ/operando ICP-MS. K. H. Chae performed the XANES/EXAFS analysis. Y. J. Hwang and B. K. Min provided an idea for the electrochemical analysis. P. Strasser and H. -S. Oh supervised the research and wrote the manuscript. All authors reviewed the manuscript.

Declaration of Competing Interest

The authors declare no competing financial interests.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2020.118820.

References

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Appendix A. Supplementary data

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