Highly selective and scalable CO$_2$ to CO - Electrolysis using coral-nanostructured Ag catalysts in zero-gap configuration

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ABSTRACT

The direct electroreduction of CO$_2$ to pure CO streams has attracted much attention for both academic research and industrial polymer synthesis development. Here, we explore catalytically very active, coral-structured Ag catalyst for the generation of pure CO from CO$_2$-feeds in lab-bench scale zero-gap CO$_2$ electrolyzer. Coral-shaped Ag electrodes achieved CO partial current densities of up to 312 mA cm$^{-2}$, FE$_{CO}$ of 38%, and FE$_{CO}$ clearly above 90%. In-situ/operando X-ray Absorption Spectroscopy revealed the sustained presence of Ag$^+$ subsurface species, whose local electronic field effects constitute likely molecular origins of the favorable experimental kinetics and selectivity. In addition, we show how electrode flooding in zero-gap CO$_2$ electrolyzer compromises efficient CO$_2$ mass transfer. Our studies highlight the need for a concomitant consideration of factors related to intrinsic catalytic activity of the active phase, its porous structure and its hydrophilicity/phobicity to achieve a sustained high product yield in AEM zero-gap electrolyzer.

1. Introduction

With the increasing demand for reducing the CO$_2$ emissions caused by global greenhouse gas effect, electrochemical carbon dioxide reduction reaction (CO$_2$RR) has been considered as a key technology for achieving a sustainable and clean society [1–4]. The electrochemical reduction of CO$_2$ using renewable electricity is an important future CO$_2$-to-fuels/chemicals process, which converts the greenhouse gas CO$_2$ directly into useful chemicals, polymer precursors, and fuels, such as carbon monoxide (CO), acetaldehyde, ethylene, and ethanol [5–10]. To increase the economic feasibility of CO$_2$RR, new approach has been proposed including co-electrolysis coupling CO$_2$RR with organic oxidation reactions (OOR) instead of oxygen evolution reaction (OER) [11]. The OOR produces more economical valuable products such as 2,5-furandicarboxylic acid (FDCA) and ethyl acetate, suggesting possibility of CO$_2$RR technology. Among cathodic CO$_2$RR products, CO is currently the product of highest economical and commercial interest and priority, due to its high market value and moderate faradaic requirement of merely two electrons [12,13]. However, the CO$_2$RR faces formidable obstacles with respect to commercialization due to its low efficiency and poor selectivity. To overcome this problem, tremendous efforts have been devoted to identifying an efficient and selective catalyst for the CO$_2$RR to CO.

Prior studies on the CO$_2$ to CO electroreduction using H-cell configurations and CO$_2$ saturated liquid electrolytes have focused on the catalytic properties of a wide range of materials [14–19]. Among them, Ag is known to achieve a high efficiency toward CO$_2$-to-CO, because of the weak CO chemisorption energy on the surface and poor binding energy of atomic hydrogen, which results in a poor competing catalytic activity of the hydrogen evolution reaction (HER) [20,21]. Recent...
studies reported that nanostructured Ag catalyst and partial charged Ag-based materials such as oxygen bonded Ag and Cl adsorb Ag exhibit a higher CO$_2$RR activity and faraday CO efficiency (FE) than plain Ag catalyst in aqueous condition [22–28]. Nanostructured and charged Ag surface enhance local electronic fields. The enhanced electronic fields stabilize polarized CO$_2$RR intermediates, improving CO$_2$RR activity. The experimental current density of the CO$_2$ to CO process, however, is fundamentally restricted to under 30 mA cm$^{-2}$ in H-type electrolyte due to the low solubility of CO$_2$ in the aqueous electrolyte and the resulting mass transfer limitations [29,30]. To increase the limiting catalytic current density, CO$_2$ electrolysis systems typically utilize gas-diffusion layer (GDL) electrodes. Kenis et al. reported on an electrolytic flow reactor, which incorporated a Gas Diffusion Electrode (catalyzed GDL, also referred to as Porous Transport electrode, PTE) that separated the CO$_2$ gas flow channel and the liquid catholyte flow compartment on the cathode side [31–34]. Using this gas/liquid flow CO$_2$ cathode, they obtained a current density as high as 440 mA cm$^{-2}$ with an FE$_{\text{CO}}$ of over 90% using a Ag catalyst operating in 3 M KOH electrolyte [35]. Also, a supported gold catalyst was used to achieve CO$_2$RR with a high current density (158 mA cm$^{-2}$) and a high Faradaic efficiency for CO (FE$_{\text{CO}}$ 85%) in alkaline condition in the same flow cell [34]. Sargent and coworker have used a gas/Liquid reactor similar to that used by Kenis group to attain an improved CO$_2$to-CO efficiency under high pressure and high alkaline reaction environments. They reported high energetic efficiencies (>80%) for CO production at 300 mA cm$^{-2}$ [35].

The gas/liquid flow electrolyzer cathodes suffer from scalability and display practical difficulties in efficiently handling the three-phase interface, which is a major limitation for commercialization. Masel et al. reported about a simplified, “zero-gap” CO$_2$ electrolysis device that uses an anion exchange membrane (AEM, Sustainion$^{TM}$) with humidified CO$_2$ flow in the cathode and exhibits a current density of 200 mA cm$^{-2}$ with steady FE$_{\text{CO}}$ of over 90% using Ag catalyst [36]. The zero-gap CO$_2$ flow AEM-type electrolyzer cell (denoted as AEM zero-gap electrolyzers) is currently considered as a very promising configuration due to its zero-gap structure between catalyst and solid membrane thereby minimizing ohmic resistances, which has already been proven to be commercially available through a fuel cell and electrolyzer system [37]. Recently, various catalysts used in AEM zero-gap electrolyzers have been reported to exhibit excellent FE and current density for CO$_2$RR [38–40]. However, only very few studies were focused on exploring the correlation of cathode structure and efficiency in the CO$_2$ flow AEM zero-gap electrolyzer.

In this study, we report on the electrochemical activity and stability of a nanostructured Ag-based Gas Diffusion Electrode incorporated in an AEM zero-gap CO$_2$ electrolyzer. We introduce a novel nanostructured, coral-shaped Ag catalyst material and characterized it first in a liquid electrolyte H-cell environment and followed by the CO$_2$ electrolyzer studies. What sets this Ag nanocoral electrolyt catalyst apart from other Ag catalyst lies in its direct deposition onto the Gas Diffusion Layer and high active surface area that results in highly favorable catalytic selectivities [23]. Also, the coral-structured Ag electrode inherently demonstrated a high catalytic activity thanks to its high microporosity that aided in improving CO$_2$ mass transfer, affording high partial CO current density of 300 mA cm$^{-2}$ with high FE$_{\text{CO}}$ (>95%) at largely reduced Ag loading. Using in-situ/operando X-ray adsorption fine structure (XAFS) analyses combined with contact angle measurements performed before and after the durability test, we revealed that the e-Ag catalysts enhanced the hydrophobic properties under prolonged CO$_2$ electrolysis. This led to gradual electrode flooding and hence to a decline in experimental FE$_{\text{CO}}$. Exemplified by the present high-performance, nanostructured Ag catalyst, we further conclude that control of the catalyst hydrophobicity is as important a factor for catalytic activity and selectivity as is morphology or composition zero-gap CO$_2$ flow, and must be taken into consideration in the preparation of Gas Diffusion Electrodes for CO$_2$ Electrolyzers.

2. Results and discussion

2.1. Morphology and chemical state of e-Ag coral electrode

Silver catalyst layers were deposited on polytetrafluoroethylene-coated carbon paper using an e-beam irradiation technique (denoted as e-Ag electrodes). The Ag layers grew well onto the carbon paper such that their contact resistance was minimized. As prepared, the Ag layers showed a highly condensed morphology with low porosity (Fig. 1a and c). Additional Ag black electrodes, which were manufactured at 70 °C by spraying commercial Ag nanoparticles on carbon-based GDL served as control catalysts; they showed severe agglomeration with a microporous structure (Fig. S1). Transmission electron microscope (TEM) images (Fig. S2) revealed that the commercial Ag particles had round shapes with an average particle size of 50–100 nm.

Nanostructured e-Ag coral electrodes were synthesized starting from deposited e-Ag electrodes using a two-step electrochemical method [23]. The e-Ag electrode was oxidized in Ar-saturated 0.1 M KCl solution at 0.3 V (vs. Ag/AgCl, 3 M KCl) for 12 h, resulting in its conversion to condensed AgCl (Fig. S3). Then, the AgCl electrode was reduced in CO$_2$-saturated 0.1 M KHC0$_3$ solution at −1.2 V (vs. Ag/AgCl, 3 M KCl) for 30 min to generate the final e-Ag coral electrode. As shown in Fig. 1b and d, the electrochemical procedure resulted in a coral-like nanoporous structure, which favored gas transfer. The energy-dispersive X-ray (EDX) elemental mapping (Fig. 1e) revealed largely Ag and a small amount of Cl in the catalyzed portion of the GDE, suggesting the coexistence of residual Cl$^-$ ions in the electrode.

The detailed morphological difference of the prepared Ag-based electrodes was further studied by electrochemically active surface areas (ECSA) and gas permeability. The ECSA was calculated by capacitance measurements in CO$_2$ saturated 0.5 M KHC0$_3$ solution at different scan rate and the results are shown in Fig. S4. The calculated ECSA of e-Ag coral electrode is 2.368 m$^2$, which is higher than that of Ag black electrode (0.824 m$^2$) and e-Ag electrode (0.164 m$^2$). This result clearly indicates the highly porous structure of e-Ag coral electrode. Fig. S5 shows the N$_2$-based gas permeability of the prepared Ag electrodes, which further reveals the not only the porosity of electrode but also the degree of mass transfer of CO$_2$ gas in the CO$_2$RR. The gas permeability of the prepared electrodes was evaluated by measuring N$_2$ gas permeation, and the results are shown in Fig. S5. The e-Ag coral electrode showed gas permeability of 19.01 × 10$^{-13}$ m$^2$, which was higher than 18.57 × 10$^{-13}$ m$^2$ of Ag black electrode and 17.257 × 10$^{-13}$ m$^2$ of e-Ag electrode. These results show that e-Ag coral has high ECSA and improved gas permeation.

The crystal structure transformation that occurs during the electrochemical generation of the coral shapes was investigated using the in-situ X-ray diffraction (Fig. 2a). The crystalline metallic Ag was converted to crystalline AgCl in 0.1 M KCl solution, which was then transformed into metallic Ag with coral-like nanoporous structure in the CO$_2$-saturated 0.1 M KHC0$_3$ solution. This reveals that the initial AgCl was dissolved into Cl$^-$ ion and Ag$^{+}$ cation. The dissolved Ag$^{+}$ then re-nucleated and formed the final metallic e-Ag coral structure. The crystalite size of Ag is calculated by in-situ XRD peak using Scherrer’s equation to confirm morphology transform. The crystal size of e-Ag electrode is 88.5 nm, which is decreased to 36.5 nm of e-Ag coral crystallite size after electrochemical treatment, further confirming morphology transform to nanostructured e-Ag coral. The detailed chemical states of the e-Ag coral were also examined using depth-resolved X-ray photoelectron spectroscopy (XPS) (Fig. 2b). The Ag black electrodes and initial e-Ag electrode comprised zero valence Ag elements (Fig. S6). After oxidation, the e-Ag electrode was fully converted to Ag$^+$, which was then back converted to AgCl. This finding agrees with those obtained from XRD. With reduction condition in the CO$_2$-saturated 0.1 M KHC0$_3$ solution, the AgCl electrode was converted to e-Ag coral electrode. The outermost layer of the e-Ag coral structure (KE 300 eV) was changed to metallic Ag, while the near-surface of the e-Ag coral (KE 1100 eV) was softly
oxidized. In the Cl 2p core level spectrum (Fig. S7), the 2p$_{3/2}$ binding energies of surface Cl at 198 eV were assigned to commercial AgCl (Fig. S8), revealing very small amount of Cl ion adsorbed by the e-Ag coral surface. In contrast, the near-surface of the e-Ag coral showed Cl 2p$_{3/2}$ peaks at 197 eV, a similar binding energy to that observed in the electrochemically synthesized AgCl electrode in this study, suggesting that some synthesized AgCl species remained after reduction in CO$_2$-saturated 0.1 M KHCO$_3$ solution. In a control experiment, where an Ag black electrode was subject to the electrochemical procedure to generate coral shapes (denoted as 'Ag black coral electrode'), a large amount of AgCl remained, and the morphology was highly agglomerated (Fig. S9).

2.2. Electrocatalytic activity of the prepared Ag electrodes for CO$_2$ reduction in the zero-gap CO$_2$ flow electrolyzer

The catalytic electrochemical CO$_2$RR performances of the Ag electrodes were measured using an electrochemical H-cell in CO$_2$-saturated 0.5 M KHCO$_3$ and a zero-gap CO$_2$ Gas Diffusion Electrode flow electrolyzer (Fig. 3 and S10). The H-type cell is a traditional electrochemical system, in which the anode and cathode are separated by a polymer anion exchange membrane (AEM) and filled with CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte [41]. By contrast, AEM zero-gap CO$_2$ flow electrolyzer used humidified CO$_2$ as a cathode reactant instead of...
CO₂-saturated electrolyte to increase the upper limit of CO₂ mass transfer. Fig. 3a shows the detailed system of the AEM zero-gap CO₂ flow electrolyzer with reference electrode. 1 M KOH was fed to the Pt coated Ti flow plate and IrO₂ electrode in the anode side for oxygen evolution reaction, and humidified CO₂ was directly fed to the carbon flow plate and Ag-based electrode in the cathode side for CO₂RR. The AEM was located between IrO₂ and Ag-based electrode, enabling the zero-gap structure of AEM CO₂ flow electrolyzer.

First, in the H-type electrochemical cell with CO₂ dissolved in an aqueous electrolyte, the e-Ag coral electrode showed higher total and CO partial current densities than the other Ag electrodes (Fig. 3b). The highest CO partial current density on the e-Ag coral electrode was 2.7 mA cm⁻², whereas those of the e-Ag electrode and Ag black electrode were 1.6 and 1.8 mA cm⁻², respectively (Fig. 3c). The e-Ag coral and Ag black electrode showed a maximum FEₐ of >95%, while the e-Ag electrode only shows a maximum FEₐ of 79.0% (Fig. 3d). In contrast, in the zero-gap CO₂ flow electrolyzer tests, the observed current density was generally much larger, and the differences between the individual electrode catalytic CO₂RR activities was much more significant (Fig. 3e). Now, the maximum CO partial current density of the e-Ag coral electrode in the zero-gap CO₂ flow was 312 mA cm⁻² at −0.79 V vs. RHE compared to a mere 2.7 mA cm⁻² at −1.08 V vs. RHE in the H-type cell. Moreover, the FEₐ of all the Ag-based electrodes in the electrolyzer cells were essentially 100% in the 2.5–3.5 V cell voltage region, which underlined their favorable efficiency with zero-gap CO₂ flow. At larger cell voltages, the FEₐ declined due to increasing rates of the HER, as shown in Fig. 3f and g. The CO₂RR electrocatalytic performances in this work are compared with other previously reported reports (Table S1), and show obviously advantages. Based on these results, the zero-gap CO₂ flow electrolyzer represents higher current density, lower overpotential and higher FEₐ than those of H-type cell, indicating that the zero-gap CO₂ electrolyzer is a more efficient strategy to achieve levels.

Over the cell voltage range considered here, the e-Ag coral electrode consistently showed a higher CO₂RR performance and energy efficiency than the Ag black and e-Ag electrodes (Fig. S11). CO Energy efficiency (EEₐ) was highly affected by cell voltage and FEₐ under CO₂RR operation. EEₐ decreases with increasing current density due to increasing cell voltage. At high current density, drastically decreased EEₐ is observed owing to reduction of FEₐ. The e-Ag coral electrode exhibits lower cell voltage at same CO partial current density than Ag black and e-Ag electrodes, leading highest EEₐ (38% for CO partial current density of 312 mA cm⁻²). Especially in the low cell voltage region, the e-Ag coral exhibited superior CO₂RR performance compared to other electrodes, suggesting an intrinsically higher catalytic activity of the Cl⁻ modified Ag materials compared to metallic Ag [42]. The performance of the Ag black electrode was, in turn, superior to that of the "e-Ag electrode", despite their similar chemical states (metallic Ag), suggesting that the morphology of the Ag catalyst is severely influencing the CO partial current density. A key morphological difference that may in part explain the observed performance difference is the distinctly larger microporosity of the e-Ag coral and Ag black electrodes compared to the e-Ag electrode. This facilitates CO₂ mass transport and enables larger CO partial limiting current densities.

To examine the influence of Ag loading in the zero-gap CO₂ flow electrolyzer, the CO₂RR performance of Ag black and e-Ag coral electrodes was evaluated with different Ag loading amounts. The corresponding results are shown in Figs. S12 and S13, respectively. These results demonstrated an initial gradual increase in the CO partial currents with loading until a maximum current was reached. The current
densities of all Ag-based electrodes increased exponentially with an increase in the cell voltages at low potential regions, but converged to a maximum current at high voltages. The gas permeability of Ag black electrodes with different Ag loadings was measured, and the gas transfer decreased as the loading amount of Ag increased and the thickness of the electrodes with different Ag loadings was measured, and the gas transfer decreased in the cell voltages at low potential regions, but converged to a maximum current at high voltages. The gas permeability of Ag black electrodes in the bulk. The strong bulk sensitivity of the XANES technique is a plausible reason why it was not able to detect the presence of oxidized near-surface Ag species in conjunction with Cl ions in the Ag black coral electrode. The linear combination fitting of measured XANES spectra was carried out to compensate for the above issue. In additional, in-situ/operando XANES analysis was performed in the zero-gap CO2 flow electrolyzer to observe changes in the electronic structure under real working conditions. Fig. S16 shows that a small opening was inserted on the cathode endplate of the zero-gap CO2 flow electrolyzer to enable X-ray illumination of the Ag-based electrodes. The in-situ/operando XANES and extended X-ray absorption fine structure (EXAFS) analysis evidenced that the Ag black and e-Ag coral electrodes turned largely into metallic Ag under CO2RR conditions (Figs. S17 and S18). However, a detailed XANES linear combination fitting (LCF) analysis using Ag foil (Ag0) and AgCl (Ag+) as the standards, (Fig. S19), also revealed some significant differences between the Ag electrodes (see Fig. 4b). For Ag+, AgCl was used as Ag+ reference in LCF fittings because Ag2O was not matched with XANES results. The LCF indicated a presence of a varying amount of Ag+ species. Under open circuit voltage conditions, both electrodes exhibit highly metallic properties with only 2-2.9% of Ag+ species. When the applied cell voltage was raised to 2.0 V, the Ag+ species ratio of Ag black electrode slightly increased to 5.4%, while the Ag+ component of e-Ag coral increased sharply to 12.5%. When the voltage was increased further to 3.0 V and 4.0 V, the Ag+ species of Ag black electrode increases to 14.0% and declines marginally to 13.8%. In case of e-Ag coral, the Ag+ species ratio elevates up to 17.4% and declines marginally to 13.8%.

The observed Ag+ species in the LCF analysis can be explained using the terms of local electric fields. The effect of electric fields on electrochemical CO2-to-CO has been investigated by Roldan Cuenya and other research groups [43-45]. They reported that the negative electric fields at Ag catalysts reduce the thermodynamic and kienetic barrier of CO2RR to CO by enhancing COOH* binding and, at the same time keeping CO* binding constant. For the e-Ag coral, it possesses Cl- species at near-surface which increases negative dipole moments of surface Ag, resulting in intrinsic local electric fields [42,46]. At cell voltages of 2.0 V and 3.0 V, e-Ag coral electrode has abundant Ag+ species than Ag black electrode, suggesting that the local electric fields of e-Ag coral were highly enhanced by the applied external electric field. Furthermore, the e-Ag coral structure with large number of under-coordinated Ag and defects is affected to enhance the negative electric field [43,47]. Interesting, the amount of Ag+ species in the Ag electrodes at 4.0 V was

![Fig. 4](https://example.com/fig4.png)  
**Fig. 4.** Electronic structure of Ag-based electrodes during CO2RR in the zero-gap CO2 flow electrolyzer. (a) X-ray absorption near edge structure (XANES) spectra of Ag K-edge for the synthesized electrode and reference materials. (b) in-situ/operando XANES linear combination fitting results of Ag black and e-Ag coral electrode. Scheme of effect of electric fields for CO2RR to CO with respect to (c) Ag black and (d) e-Ag coral electrodes at a cell voltage of 2.0 V, estimated by the in-situ/operando XANES results.
maintained or slightly reduced compared to 3.0 V, which may be affected by the saturation of the electric field and the change of electrode structure. Based on these results, it can be explained that the high CO$_2$RR catalytic activity of e-Ag coral electrode attributed to the enhanced electric fields during applied potential.

2.4. Stability test of e-Ag coral electrode in the zero-gap CO$_2$ flow electrolyzer

To test the feasibility of the coral-shaped Ag electrode for sustained CO$_2$RR in a zero-gap CO$_2$ flow electrolyzer, a longer-term durability test was conducted under chronopotentiometric conditions at an applied constant current of 1 A across a 10 cm$^2$ active geometric electrode area. The results of this test are shown in Fig. 5. The cell voltage of the e-Ag coral electrode remained at $\sim$2.75 V for 30 h, with some fluctuations occurring at 19 h. The FE$_{CO_2}$ values remained stable at 95% until 10 h and then gradually decreases to 70% after 19 h test time. After a period of more pronounced electrode potential and cell voltage fluctuations, the e-Ag coral electrode returned to a stable FE$_{CO_2}$ of over 95%, suggesting that the transient decline in CO FE during the test period of 10–19 h was due to cell operational problems and not due to a chemical degradation of e-Ag coral electrode itself. We have evidence that electrolyte flooding is the cause of this decline in FE, which blocked the supply of CO$_2$ gas, creating an environment similar to that of the H-type electrochemical cell. Flooding would strongly reduce the interfacial CO$_2$ concentration and promotes the HER reaction. After 19 h, the condensed water in released from the electrode and FE$_{CO_2}$ is recovered. To confirm the effect of flooding on potential fluctuations, 10 ml of DI water was added directly to the cathode at a current density of 100 mA cm$^{-2}$ (Fig. S20). After this addition, the cathode and anode potentials indeed drastically varied due to flooding. As flooding progressed, the local distribution of the cathode reaction was uneven, as the mass transfer of CO$_2$ was partially blocked, affecting potential of the anode [48]. After a few minutes, the anode potential fluctuation was again observed due to the overflow and removal of the electrolyte at the electrode, which shows that FE$_{CO_2}$ was returned by recovery from flooding when cell voltage fluctuation occurs at 19 h. To support our flooding hypothesis further water contact angle measurements of the Ag catalysts were carried out to clarify the degree of hydrophobicity and hydrophilicity of each electrode (Fig. 5b and S21). Ag black and e-Ag electrode exhibited high contact angles, showing the hydrophobic nature owing to their metallic property, whereas the e-Ag coral electrode displayed a lower contact angle, indicating enhanced surface hydrophilicity, conceivably due to the presence of anions on the surface.

The results underline the detrimental role of pore flooding in CO$_2$ Gas Diffusion Electrodes [49], yet, more generally, remind us of electrode flooding issues in any gas consumption electrodes, e.g. the oxygen reduction cathodes of fuel cells, where water management is a similarly critical issue that affects performance and durability [50,51]. In the zero-gap CO$_2$ flow electrolyzer for CO$_2$RR, presence of water at the cathode is necessary, owing to the activation of anion exchange membrane and proton source of CO$_2$RR. However, excess water blocks the mass transfer of CO$_2$ and accelerates HER, leading to the decline in FE$_{CO_2}$. Moreover, alteration of the hydrophobicity of metallic Ag into a more hydrophilic state appears quite undesirable owing to negative dipole moments of surface Ag during CO$_2$RR, as it renders the cathode more vulnerable to flooding [52]. As a result of this, we propose that Ag-based electrodes should be prepared with a rather hydrophobic character to maximize the CO partial current density and time-stable CO production through efficient CO$_2$ mass transfer.

3. Experimental section

3.1. Materials

KOH, KHCO$_3$, and KCl were purchased from Sigma Aldrich. Silver foil (Alfa Aesar), AgO (Sigma Aldrich), and AgCl (Sigma Aldrich) were used as the standards of XANES and XPS analysis. All chemicals were used without further purification. Silver nanopowder (Sigma Aldrich) was used as the catalyst for CO$_2$RR. The Ultrapure water (>18 mΩ) was supplied by Arumi mini lab water system (Sartorius). The carbon paper (Sigracet 39 BC) was used as a GDL. The anion exchange membrane (Dioxide Materials) was used for the single cell test.

3.2. Preparation of e-Ag coral electrode

A thin Ag layer was deposited on a carbon paper-based gas diffusion layer (GDL, Sigracet 39 BC) using the electron-beam (e-beam) evaporation (ULVAC), which is denoted by the e-Ag electrode. The e-Ag coral electrode was synthesized using KCl solution by employing a method suggested in one of the previous reports [23]. The e-Ag electrode was oxidized in the Ar-saturated 0.1 M KCl solution at 0.3 V (vs. Ag/AgCl) for 12 h. The e-Ag coral electrode was fabricated by reducing the oxidized e-Ag electrode in the CO$_2$-saturated 0.1 M KHCO$_3$ solution at $\sim$1.2 V (vs. Ag/AgCl) for 30 min. Afterward, it was rinsed using DI water.

3.3. Preparation of Ag black electrode

The Ag black electrodes were manufactured by spraying the catalyst ink onto the carbon paper (Sigracet 39 BC). The catalyst ink was ultrasonically mixed with isopropyl alcohol (2 mL), 5 wt% of Nafion solution (5 wt% target of Ag nanoparticle) and commercial silver nanopowder (60 mg). The prepared ink was sprayed onto the GDL at 70 °C. The electrode area was 10 cm$^2$.

3.4. Preparation of IrO$_2$ electrode

The catalyst ink was ultrasonically mixed with isopropyl alcohol (2 mL, Sigma-Aldrich), 5 wt% of Nafion solution (5 wt% target of IrO$_2$ nanoparticles, Sigma-Aldrich), and commercial IrO$_2$ nanopowder (60 mg, Alfa Aesar). The prepared ink was sprayed onto the GDL (Sigracet 39 BC) at 70 °C using a homemade heating vacuum plate. The loading of IrO$_2$ was fixed at 1.0 mg cm$^{-2}$, and the electrode had a circular 10 cm$^2$
3.5. Electrochemical CO₂ reduction in electrochemical H-cell

Two-compartment electrochemical H-cell made of polyether ether ketone (PEEK) was used to measure CO₂RR performance of the electrode. A Selenium anion exchange membrane was employed to separate anode and cathode compartment. Ag/AgCl electrode (Basi, 3 M NaCl) and glassy carbon electrode were used as reference electrode and counter electrode, respectively. 20 ccm CO₂ gas purged to 0.5 M KHCO₃ electrolyte. CO₂RR activity was measured with chrono-amperometry at each fixed potential for 30 min. The gas product was analyzed by the gas chromatograph (GC, Agilent 7890A).

3.6. Electrochemical CO₂ reduction single cell test

A detailed schematic of an AEM zero-gap CO₂ electrolyzer is described in Fig. 3a. The catalyst coated electrode (CCE) method was used to fabricate membrane electrode assemblies (MEAs). The active area of all MEA was 10 cm². Synthesized electrode and commercial IrO₂ (Alfa Aesar, 1.0 mg cm⁻²) electrode were used as the cathode and anode electrodes for the single cell test, respectively. Before assembly, the anion exchange membrane (AEM, Dioxide materials, X37-50) was pretreated in 1 M KOH solution for 48 h and washed with DI water several times. The MEA was mounted onto a custom-made single cell with pin-type channels for anode and serpentine channel for cathode. 100 ccm of the reactant gas (CO₂) humidified at 50 °C was fed to the cathode side, and the 1 M KOH solution was supplied to the anode side. Electrochemical experiments were conducted using a VSP potentiostat (Bio-Logic) with a 10 A booster at room temperature. To measure the ohmic resistance, an impedance analysis was conducted at 2.0 V over the frequency range of 0.1–1 kHz. The Ag/AgCl (3.5 M KCl) reference was adopted for the anode flow line to detect the anode potential. The cathode potential was calculated using the following equation:

\[
\text{Cell voltage}\ =\ \text{Anode potential}\ -\ \text{Cathode potential}\ -\ iR
\]

where R is the ohmic resistance obtained by the impedance measurement. The gas chromatograph (GC, Agilent 7890A) was used for analyzing the composition of the output gas. GC was connected online with the water trap, which was attached to the outline of cathode. Ultra-high pure He gas (99.9999%) was used as the carrier gas. A flame ionization detector (FID) with a methanizer and a thermal conductivity detector (TCD) were installed in the GC. The TCD detects the hydrogen gas, while the FID detects the hydrocarbon product (CO and CH₄). A methanizer was used to enhance the detection of CO by FID. The Faradaic efficiency of hydrogen and hydrocarbon product were calculated using the following equation:

\[
FE_{\text{product}}(\%) = \frac{i_{\text{produced}}}{i_{\text{total}}} \times 100 = \frac{V_{\text{produced}} \times Q \times 2p}{i_{\text{total}}} \times 100 \ iR
\]

where Q is the flow rate of CO₂, F is the Faradaic constant, p is the pressure, T is the room temperature, and R is the ideal gas constant with a value of 8.314 J mol⁻¹ K⁻¹. The total current was measured by the VSP potentiostat, and the partial currents of the product were calculated from the volume of the product, which was obtained by the GC chromatogram peaks.

The energy efficiency of zero-gap CO₂ flow electrolyzer was calculated by following equation:

\[
EE_{\text{CO}_2}(\%) = \frac{(1.23) - (-0.109)}{\text{Cell voltage} (V)} \times FE_{\text{CO}_2}(\%)
\]

1.23 V and −0.109 V are the thermodynamic potential of water oxidation reaction and CO₂RR to CO₂, respectively. Cell voltage is voltage of the zero-gap CO₂ flow electrolyzer during operation. FE₂ is measured by GC.

3.7. Physical characterization

The SEM images and EDX elemental mapping were obtained from Regulus 8230 (Hitachi) at an operating voltage of 5 kV. The TEM measurements were conducted using the Talos F200X (FEI) at an operation voltage of 200 kV. The XRD patterns were collected using the Empyrean (Malvern Pananalytical) with a Cu K-alpha X-ray source. Gas permeability was measured by Capillary flow porometer at maximum 2 atm. (PMI, CFP-1500AE). The XPS spectra were measured using PHI 5000 VersaProbe (Ulvac-PHI) and 4D beamline of Pohang Accelerator Laboratory (PAL), Pohang, South Korea. The operando X-ray absorption spectroscopy was performed using custom made single cell with 10C beamline of PAL. All samples were measured in fluorescence and transmission modes.

4. Conclusions

We have prepared, characterized and tested a catalytically highly active nanostructured coral-shaped Ag (e-Ag coral) electrode for the generation of pure CO streams using zero gap CO₂ flow cell electrolyzer. We compared its electrochemical performance to those of a reference e-Ag electrode and a reference Ag black electrode. In an H-type electrochemical cell, the e-Ag coral electrode exhibited a low CO partial current density of only 2.7 mA cm⁻² with a CO maximum Faradaic efficiency of 90.3%. In the zero-gap CO₂ flow electrolyzer, a high CO FE of >95% and a high CO partial current density of 312 mA cm⁻² was achieved by the e-Ag coral electrode with an Ag loading amount of 0.5 mg cm⁻². Detailed characterization of the chemical state of the catalysts under reaction conditions suggested that the enhanced CO₂RR performance of e-Ag coral electrode may be accounted for in part by the presence of Cl⁻ modified Ag⁺ species near the surface (an electronic reason for enhanced catalytic activity), and also in part by the presence of a large microporosity (mass transport reason for higher current densities). An in-situ/operando Ag K-edge XAFS analysis revealed that the Cl-doped-Ag coral surface with a large number of defects and under-coordinated Ag possess enhanced negative electric fields, leading low overpotential for CO₂ reduction to CO. The cell voltage of e-Ag coral electrode remained stable at 2.75 V for 30 h under a current of 1 A within a cell area of 10 cm². However, FE₂ decreases abruptly at 19 h owing to flooding, which is associated with the hydrophilicity of e-Ag coral and negative dipole moments of surface Ag. Moreover, flooding can act as an obstacle for the mass transfer of CO₂, as it reduces the CO partial current density. Thus, it was clear that the hydrophobicity of the electrode was important to prevent the flooding by suppressing the HER and improving mass transfer of CO₂. Our study can provide a novel insight for understanding CO₂RR in zero-gap CO₂ flow electrolyzer. It presents a novel strategy to design advanced electrodes to achieve a high current density and high durability by introducing not only an intrinsic catalytic activity but also a porous structure and hydrophobicity.

Declaration of competing interest

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

CRediT authorship contribution statement

Woong Hee Lee: Conceptualization, Methodology, Writing - original draft, Formal analysis. Young-Jin Ko: Conceptualization, Resources. Yongjiu Choi: Formal analysis, Resources. Si Young Lee: Formal analysis, Resources. Chang Hyuck Choi: Methodology, Resources. Yun Jeong Hwang: Formal analysis, Resources. Byoung Koun Min: Formal analysis, Resources. Peter Strasser: Writing - review & editing,
Supervision: Hyung-Suk Oh: Writing - review & editing, Supervision.

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Appendix A. Supplementary data

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