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An Ir-based anode for a practical CO_2 electrolyzer

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ABSTRACT

The electrochemical conversion of CO_2 to fuels may provide a two-fold benefit of reducing CO_2 emissions while providing of means of storing excess energy generated from renewable sources in a chemical form. Recent research focuses primarily on the development of efficient CO_2 reduction electrocatalysts, while little attention has been given to the development of an effective oxygen evolution anode that is compatible for practical CO_2 electrolyzers. In this report, we investigated potential anode candidates that are highly active for oxygen evolution and structurally stable under near-neutral operation conditions for a typical CO_2 electrolyzer. The majority of non-precious metal-based catalysts are unstable in neutral bicarbonate electrolytes during CO_2 electrolysis. In contrast, iridium-coated porous titanium electrodes exhibited decent oxygen evolution reaction activities as well as excellent stability under near-neutral conditions. Furthermore, by spray coating iridium black nanoparticles onto a cation exchange membrane (Nafion 211) and coupling it with a state-of-the-art nanoporous Ag catalyst as the CO_2 reduction cathode, a remarkable total current of ~375 mA at an applied cell voltage of 2.6 V in the span of 24 h was achieved using a 25 cm^2 CO_2 electrolyzer flow cell.

1. Introduction

Renewable energies, such as solar and wind, are potential energy sources for a green and sustainable energy future. However, a major challenge of renewable energies is that they are variable in nature and therefore, the power generation from renewable sources varies over time. A solution to compensate for these variabilities is to power an electrochemical device to transform CO_2 into value-added products such as CO by using renewable energy that provides a mean to store excess energy in a chemical form. The produced products such as CO can then be used in the well-established Fisher-Tropsch process or other gas-to-liquid processes to make synthetic fuels and chemicals; and thus, this will provide an economic viable pathway for renewable energy sources to gain revenue while simultaneously reducing CO_2 emissions and dependency on fossil fuels [1–3].

Over the last decade, there have been significant efforts in developing catalysts that can convert CO_2 molecules to useful chemicals in an efficient way. Bulk metals have been studied intensively as CO_2 reduction electrocatalysts and various efforts have been made into designing high performing nanostructured electrocatalysts with high selectivity towards a desired product [4,5]. For example, Lu et al. have developed a nanoporous Ag (np-Ag) catalyst with monolithic structure that can achieve exceptionally high activity of approximately 20 mA cm^{-2} in aqueous electrolyte with over 90% selectivity towards CO_2 reduction to CO at a moderate potential of 0.6 V vs the reversible hydrogen electrode (RHE) [6]. However, the majority of these efforts focused only on the cathode side (i.e. CO_2 reduction electrocatalyst) and little consideration was given to the whole CO_2 electrolysis process, such as the choice of electrolyte, the delivery of CO_2 reactant to active sites, and product separation. A good understanding of the whole process is required to develop a practical CO_2 electrolyzer for industrial applications.

The existing designs of CO_2 electrolyzers range from microfluidic flow cells to polymer-membrane based reactors [7–10]. Each configuration has been shown certain advantages and disadvantages compared to others. As CO_2 reacts strongly with bases and an acidic electrolyte promotes undesired hydrogen evolution reaction, a neutral pH environment is the most popular choice of current CO_2 electrolysis research. In order to operate a CO_2 electrolyzer in a neutral pH condition, it requires an oxygen evolution reaction (OER) catalyst that is stable under neutral conditions and compatible with electrolytes commonly used in evaluating CO_2 reduction catalysts. While progress has been made in developing efficient electrocatalysis for OER, the majority of these catalysts were evaluated in strong basic electrolytes (e.g. 0.1 M KOH), making these catalysts questionable whether they can be utilized in a CO_2 electrolyzer.

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Here, we investigated potential anode candidates for a practical CO_2 electrolyzer with a focus on hunting for highly active OER catalysts that operate in near-neutral conditions with good long-term stability. The investigation involves materials that have been commonly used as supports or current collectors in industrial applications such as fuel cells [11], batteries [12], and alkaline-based electrolyzers [13]. Under harsh oxidation potentials and near-neutral conditions, we identified titanium-based supports as stable materials and iridium coating significantly enhanced the OER activity, leading to a highly active and stable anode electrode that is compatible for practical CO_2 electrolyzers. Further investigations showed that a stable current of ∼375 mA for 24 h at an applied potential of 2.6 V was achieved using an Ir-based anode by directly depositing Ir black nanoparticles onto a cation exchange membrane (Nafion 211) coupled with a newly developed np-Ag cathode in a CO_2 electrolyzer flow cell.

2. Experimental methods

2.1. Materials

Stainless steel (SS), nickel (Ni), and titanium (Ti)-based electrodes were prepared by degreasing SS-mesh (400 mesh, 316, McMaster-Carr), nickel-foam (thickness: 80 μm, 346 g m^{-2}, MTI Corp.), and titanium-mesh (100 mesh, Stanford Advanced Materials) in acetone followed by rinsing in DI water. The apparent electrode size used for electrolysis was 1 cm^2. In addition, 1 cm^2 gas diffusion layer (GDL) electrodes were also prepared from Sigracet 24AA with no pretreatment.

The electrolyte used in CO_2 electrolysis studies was a 0.5 M aqueous $NaHCO_3$ solution (≥99.99%, Sigma-Aldrich). In addition, CO_2 gas (Grade 5, Keen Compressed Gas Co.) was used to purge and saturate the bicarbonate electrolyte during CO_2 electrolysis studies.

2.2. Electrode preparations

2.2.1. IrOx/Ti-mesh anode

Ir-based catalysts on freestanding Ti-based supports were constructed via a dip coating and thermal decomposition method [14]. Ti-mesh was etched for 60 min in boiling 0.5 M oxalic acid (≥98%, Sigma-Aldrich). Subsequently, the mesh were dip coated into a 10 mL isopropanol (ACS reagent, Fisher Chemicals) solution with 10% volume concentrated HCl (ACS reagent, Sigma Aldrich) containing 30 mg of dissolved $IrCl_3{\cdot}xH_2O$ (99.8%, Alfa Aesar). This was followed by drying at 100 °C for 10 min and calcination at 500 °C for 10 min in air. This procedure was repeated to achieve a catalyst loading of 1 mg cm^{-2} and the resulting materials were denoted as IrO_x/Ti-mesh.

2.2.2. Ir-CCM anode

Ir-based catalyst coated membrane (Ir-CCM) anodes were constructed via a hand-airbrush technique [15]. A catalyst ink was prepared by sonicating a slurry containing commercial iridium black nanoparticles (surface area 55–65 m^2 per gram, Premetek Co.), Nafion solution (5 wt%, DuPont), DI water, and isopropanol. The weight ratio of catalyst to dry Nafion ionomer was 4:1. The iridium containing slurry was then sprayed on to Nafion 211 that has been sandwiched between two self-adhesive Mylar laminate (DuPont) with a 25 cm^2 window. The resulting Ir-CCM anodes were dried at 40 °C for one hour. The procedure was repeated until a catalyst loading of 1 mg cm^{-2} was achieved.

2.2.3. Nanoporous Ag cathode

Nanoporous Ag cathodes were fabricated using a modified dealloying technique, which is known to be an effective method to fabricate nanoporous metals. The 40 × 5 × 5 cm^3 Ag-Al ingot used in this work was purchased from Sophisticated Alloys, Ltd (USA) and was synthesized using a vacuum induction process. This ingot was then cut in to 25 cm^2 Ag-Al precursor sheets with thickness of 500 μm using electrical discharge machining. The precursor sheets were annealed at 546 °C for 24 h and then quenched to achieve the desired solid solution phase. Subsequently, the precursor sheets were leached in 1000 mL of 5 wt% HCl for one hour, rinsed several times in de-ionized water, and then dried in a vacuum oven overnight.

2.3. Structural characterizations

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Discover diffractometer using a Cu Kα radiation source. Scans were collected in continuous mode from 20 to 80 2θ at a scan speed of 0.02°/s. Scanning electron microscopy (SEM) images were recorded on a Zeiss Auriga-60 instruments, at an accelerating voltage of 1.5 kV. Energy-dispersive spectroscopy (EDS) mapping was performed with an on-board Oxford SynergyX-MAX90 Si drift detector, with an accelerating voltage of 15 kV. A Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) System was used for analyzing the surface composition of the resulting IrO_x/Ti-mesh. The XPS data were calibrated using the binding energy of adventitious carbon at 284.5 eV and analyzed using CasaXPS software. Peaks were fitted using a blended Doniach-Sunjic and Gaussian-Lorentzian shape profile and a Shirley background [16].

2.4. Electrochemical testing

A three-electrode batch electrochemical cell was used for oxidative reaction studies. A piece of platinum wire was used as the counter electrode. The electrolyte was a 0.5 M aqueous $NaHCO_3$ solution with a pH of 8.9. All potentials were measured against an Ag/AgCl reference electrode (3.0 M KCl, BASi) and converted to the RHE scale. Electrochemical testing was performed under room temperature for >12 h in a two-compartment cell separated with an anion exchange membrane (FAA-3, Fumatech). A constant voltage was applied (chronoamperometry) and the resulting current was recorded as a function of time. All experiments were conducted using a potentiostat (Princeton Applied Research VersaSTAT 3).

For the flow cell experiments, a two-compartment electrochemical flow cell device was used with recirculating electrolytes for continuous electrochemical studies. For all flow experimental studies, np-Ag was used as the cathode. In contrast, either freestanding IrO_x/Ti-mesh or Ir-CCM was used as the anode. In addition, either a cation exchange membrane (Nafion 211, Ion power) or an Ir-CCM was used to as the compartment separator. An Autolab PGSTAT128N with 10A booster was used to control cell voltage. Constant potential electrolysis experiments were used to measure the current as a function of time.

3. Results and discussions

Conductive substrates are commonly used to support electrocatalyst particles and serve as current collectors. The investigation began with screening four common conductive substrates (i.e., 24AA GDL, Ni-foam, SS-mesh, and Ti-mesh) in a near-neutral electrolyte and the presence of a positive potential. Typical SEM images of these conductive substrates are shown in Fig. 1. All the substrates show a micron-scale porosity. The OER experiments were performed under a constant positive potential of 1.83 V versus RHE in a 0.5 M $NaHCO_3$ aqueous electrolyte with a pH value of 8.3. Fig. 2 are the OER results, which clearly show large variations in current densities for the 24AA GDL (Fig. 2a), Ni-foam (Fig. 2b), and SS-mesh