Surface generation of a cobalt-derived water oxidation electrocatalyst developed in a neutral HCO$_3^-$ /CO$_2$ system

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Water oxidation catalysis to make dioxygen and to release protons with high efficiency is a key step in the development of an artificial solar to fuel conversion device, i.e., the “artificial leaf”.\[1–3\] In combination with CO\(_2\), a potent greenhouse gas, the electrons and protons generated from water splitting can be reduced directly to nonfossil liquid fuels.\[4,5\] This method provides an attractive route for solar fuel production and avoids the problems related to hydrogen safety and storage (Figure 1).\[6,7\] The difficulty in four electron abstraction from two water molecules and simultaneous formation of an O–O bond pose a great challenge for constructing a practical device for solar fuel production on a large scale.\[8–10\] In pursuit of this, molecular complexes of precious metals such as ruthenium and iridium and their oxides along with inorganic materials derived from other transition metals have been extensively implemented and investigated in water oxidation electrocatalytic assemblies.\[10–15\] However, due to stability and performance issues the catalytic water oxidation systems are not yet capable of being used on a commercial scale and there is a constant demand for an efficient, stable and robust catalytic system derived from cheap and earth abundant materials.\[16–18\] In order to develop a liquid fuel generation system based on reductive conversion of CO\(_2\), the water oxidation catalyst (WOC) should be employed in a carbon dioxide rich environment.\[19,20\]

It is even more desirable if such a WOC would be generated in situ from a CO\(_2\) containing system and capable of performing water oxidation with high activity so that the electrons and protons obtained from the water splitting reaction may be used to reduce carbon dioxide at the cathode. Here, we report in situ formation of an efficient electro-assembled catalyst from Co\(^{2+}\) ions in an inexpensive and easy accessible neutral bicarbonate solution. In a CO\(_2\) saturated electrolyte system at near-neutral pH (pH = 6.7–6.8), the cobalt-bicarbonate-derived electrocatalyst (Co-Ci) is readily generated on conducting oxide electrode surfaces such as FTO (fluorine-doped tin oxide) and ITO (indium tin oxide), or on a glassy carbon (GC) anode and show remarkable activity for water oxidation during extended period operation (Figure 1). At 1.37 V (vs NHE) in a HCO\(_3^-\)/CO\(_2\) system at near-neutral pH, a stable oxygen evolution current density (\(j\)) of \(\approx 2.0 \text{ mA cm}^{-2}\) was obtained during constant-potential electrolysis (CPE) of water. The anodic current was sustained for many hours of electrochemical operation with no noticeable decrease in the performance. We also show that under neutral pH conditions, bicarbonate is an excellent electrolyte system that provides more stability to the electrodeposited Co-oxide derived water oxidation catalyst in comparison with the neutral phosphate buffer. As the Co-Ci is assembled in a CO\(_2\) enriched environment, the catalytic system can operate along with a carbon dioxide reduction module in the same electrochemical setup to make liquid fuel products (such as formic acid or methanol). The catalytic system also shows remarkable activity in a clean bicarbonate electrolyte (no CO\(_2\) bubbling) without having Co\(^{2+}\) in the solution. Energy-dispersive X-ray (EDX) spectroscopy shows the presence of carbon (about 30%)
in the catalyst layer and Na contents are just under 10%. This makes Co-Ci a novel and efficient electrocatalytic material for anodic water oxidation.\cite{21a} Furthermore, the Co-derived electrocatalyst presented here does not require the proton abstracting phosphate or borate buffers for electrodeposition and for anodic water oxidation, which were recently shown to be essential for the generation and activity of Co-Pi and Ni-Bi based catalysts.\cite{19,21}

The Co-Ci type electrocatalyst is generated in situ from a CO$_2$ saturated bicarbonate solution (0.1 M–1.0 M) containing Co$^{2+}$ (0.5 mM–5 mM), either on ITO or on a GC disk during the forward potential sweeps at 0 V–1.3 V (vs NHE) in a cyclic voltammetry (CV) setup (Figure 2). The cobalt-bicarbonate based electrocatalyst is also formed within seconds while keeping the potential of the working electrode above 1.2 V (vs NHE) during constant-potential experiments. Surface coverage of the electroactive species was estimated to be 7.5 nmol of the catalytic sites present per cm$^2$ of the anode.\cite{11} The electrodeposited catalytic film of Co-Ci on the ITO appears greenish and darkens on extending the CV cycles and during a prolonged CPE run (0 V–1.3 V; vs NHE). The scanning electron microscopy (SEM) image of the electrodeposited Co-Ci film is shown in Figure 3. The catalytic layer shows a surface morphology with small cracks in the film and the electrodeposits form microislands of irregular shapes and dimensions (Supporting Information Figure S3a). A magnified view of the SEM reported Co-Pi system, the onset potential for the electrocatalyst generation is at 1.15 V (vs NHE; pH = 7) on ITO.\cite{21} This indicates that the bicarbonate system initializes the electrochemical formation of a Co$^{2+}$ based water oxidation catalyst at a potential that is ≈0.2 V lower than for a phosphate electrolyte. On the other hand, on a glassy carbon substrate, a remarkable oxygen evolution current density was obtained for the Co-Ci derived electrocatalyst. The CV for the catalytic generation phase is similar to that of ITO, however, the current rapidly rises at 1.29 V (vs NHE) and reaches a value of 9.1 mA cm$^{-2}$ at just 1.60 V (vs NHE) in a CO$_2$ enriched solution (Supporting Information Figure S1). These currents are much higher than for a recently reported Cu(II)-based catalyst for water oxidation that was deposited on a glassy carbon substrate, showing a peak at 1.60 V (pH = 6.7–6.8) with $j < 0.35$ mA cm$^{-2}$ in a CO$_2$ saturated bicarbonate solution.\cite{22} In addition, the CVs show a peak current density of more than 1.15 mA cm$^{-2}$ at 1.4 V (vs NHE; pH = 6.7–6.8) in the first two scans on ITO (Supporting Information Figure S2). This peak current density for O$_2$ evolution for the Co-Ci based electrocatalyst is almost three times as high as for the Co-Pi system electrodeposited on ITO, which exhibited $\leq$0.37 mA cm$^{-2}$ at 1.4 V (vs NHE; pH = 7).\cite{21}

The cobalt-derived electrocatalyst is also formed within seconds while keeping the potential of the working electrode above 1.1 V (vs NHE) during controlled-potential experiments. Surface coverage of the electroactive species was estimated to be 7.5 nmol of the catalytic sites present per cm$^2$ of the anode.\cite{11} The electrodeposited catalytic film of Co-Ci on the ITO appears greenish and darkens on extending the CV cycles and during a prolonged CPE run (0 V–1.3 V; vs NHE). The scanning electron microscopy (SEM) image of the electrodeposited Co-Ci film is shown in Figure 3. The catalytic layer shows a surface morphology with small cracks in the film and the electrodeposits form microislands of irregular shapes and dimensions (Supporting Information Figure S3a). A magnified view of the SEM

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**Figure 2.** Top panel: Cyclic voltammetry curves for a freshly polished glassy carbon electrode in a CO$_2$ saturated 0.2 M neutral bicarbonate electrolyte with (GC/Co$^{2+}$+Ci) and without 1.0 mM Co$^{2+}$ (GC). Bottom panel: CVs for an ITO anode in a CO$_2$ saturated 0.2 M neutral bicarbonate electrolyte with (ITO/Co$^{2+}$+Ci) and without 1.5 mM Co$^{2+}$ (ITO). Scan rate: 50 mV s$^{-1}$; ITO area $A$ = 1 cm$^2$; GC disk diameter $d$ = 5.0 mm.

**Figure 3.** Enlarged view of the SEM image of the electrodeposited Co-Ci based electrocatalyst film on an ITO substrate.
shows small spherical nodules of 100–400 nm in diameter on these islands (Supporting Information Figure S3b). These nodules also grouped together to form a rosette type morphology at some locations of the film.[21,23] In a recent report for the formation of a Co-phosphate based electrocatalyst, the size of the spherical type nodule is much larger, i.e., >2 µm, and the catalytic activity was relatively low.[21] The small size of the surface structures for Co-Ci system can be related to the larger number of catalytic sites on the surface with little catalytic loading that gave rise to high anodic current densities for water oxidation.

The surface composition of the electro-deposited Co-Ci film was analyzed by X-ray photoelectron spectroscopy (XPS). The elemental detection on the XPS survey for electrodeposited Co-Ci indicates the presence of cobalt and oxygen (Supporting Information Figure S4a). The cobalt 2p (Co 2p) signals at 780 eV and 795.7 eV indicate the presence of Co²⁺ or Co³⁺ bound to oxygen (Supporting Information Figure S4a). XPS signals at 63 eV and 101 eV are also consistent with the presence of Co 3s and Co 3p in the electrodeposited Co-Ci film.[21] Likewise, the oxygen binding energies at 529.3 eV and 531 eV in Supporting Information Figure S4a are characteristic for the -OH type groups and metal bound oxides species, respectively (528–532).[23] Evidence for carbon incorporation in the Co-Ci electrodeposits is indicated by small trends for C(1s) at 286–290 eV in the XPS, which shows some contribution from carbon as C(0)O- and/or -C-OH in the catalyst (Supporting Information Figure S4a).[24] Further, the composition of the freshly electrodeposited Co-Ci layer was analyzed using energy-dispersive X-ray spectroscopy (EDX). EDX measurements show the presence of cobalt, carbon, oxygen and sodium as principle constituent elements in the Co-Ci film (Supporting Information Figure S4b). The weak response around 3.3 to 3.7 keV represents background signals from the FTO-coated glass surface. Compositional analysis of the Co-Ci EDX reveals a Co:Na ratio of 7:3:1. Hence the electrodeposited Co-bicarbonate type catalyst film has about 30 percent of carbon contents in the catalyst layer. The amount of sodium is less than 10% in the electrodeposits. Thus, the contribution of Na from electrolyte cations is much less than observed for Co-Pi where the Co:P:K ratio is 2:1:1. This makes Co-Ci a new electrocatalyst for anodic water oxidation, compared to the previously reported ones.[21a]

In order to test the long-term performance and stability of the electrodeposited Co-Ci type electrocatalyst, controlled-potential electrolysis of water was conducted in a clean HCO₃⁻/CO₂ electrolyte system (Co-Ci/HCO₃⁻/CO₂). For comparison, we also study water electrolysis with freshly prepared Co-Pi catalyst both in CO₂ saturated bicarbonate solution (Co-Pi/HCO₃⁻/CO₂) and in phosphate buffer (Co-Pi/PO₄³⁻) at neutral pH. Figure 4 shows the CPE carried out at 1.37 V (vs NHE) for the Co-Ci catalyst in a HCO₃⁻/CO₂ electrolyte system and for Co-Pi/PO₄³⁻ without cobalt ions in the solution. The Co-Ci/HCO₃⁻/CO₂ system shows a very stable oxygen evolution current density of ≥2.0 mA cm⁻² right from the beginning of the CPE operation. The Co-Ci catalyst film is very stable in HCO₃⁻/CO₂ electrolyte and there was no decrease in the catalytic performance. The electrocatalyst stays very active in bicarbonate solution during extended periods of CPE over 16 h with high current density for oxygen evolution (Figure 4). No apparent O₂ evolution current was observed on the bare ITO immersed in bicarbonate solution without cobalt ions, and the current density remains at <45 µA cm⁻² for prolonged CPE.[22] The catalyst film is stable and stays active for extended periods of CPE over 15 h with high current density for oxygen evolution. The online oxygen evolution measurements using a calibrated oxygen probe during the first 8 h show that approximately 109 µmol of molecular oxygen per cm² area of the anode surface was generated during catalytic operation (inset Figure 4). This translates to an oxygen generation rate of 0.51 mol of catalyst per second. Without the cobalt-bicarbonate catalyst in the HCO₃⁻/CO₂ system, there was no apparent O₂ evolution monitored for the bare electrode, indicated as blank (black line) in the inset Figure 4.[19] Furthermore, the in situ oxygen generation performance of the Co-Ci/ITO electrocatalyst assembly in a clean HCO₃⁻/CO₂ system was characterized with online gas chromatographic measurements. Gas chromatography analysis for a 14 h of electrocatalytic water oxidation test yields about 200 µmol molecular oxygen (Supporting Information Figure S5) with a Faradaic efficiency of 98%, considering the current was induced by 4 electron (e⁻) oxidation of water to produce one molecule of O₂. The Co-Ci electrocatalyst film is also very stable and active for anodic oxygen evolution in a clean bicarbonate solution without CO₂ saturation. The oxygen evolution current density at 1.41 V (vs NHE) approaches 3.5 mA cm⁻² and is very stable over long periods with excellent
In contrast, the Co-Pi catalyst in neutral phosphate solution shows a monotonic decrease in the anodic current density for water electrolysis during long-term CPE. At 1.37 V (vs NHE) on Co-Pi, the water oxidation initiates with a current density of about 1.65 mA cm$^{-2}$ and drops to $\geq$0.5 mA cm$^{-2}$ on the electrolysis termination (Figure 4). This indicates that in a phosphate electrolyte system, the cobalt-based electrocatalyst tends to lose its stability and performance during anodic water oxidation.

Surprisingly, the electrodeposited Co-Pi catalytic system in the neutral HCO$_3^-$/CO$_2$ system without cobalt ions appears to be more robust compared to the Co-Pi/PO$_4^{3-}$ system. The Co-Pi/HCO$_3^-$/CO$_2$ catalytic system shows a sustained current density for anodic water oxidation and there is no noticeable decrease in the catalytic oxygen evolution performance. At 1.37 V (vs NHE), the oxygen evolution current density was 1.15 mA cm$^{-2}$, which stays around 1.0 mA cm$^{-2}$ during 15 h of CPE (Supporting Information Figure S7). However, this oxygen evolution current density for the Co-Pi/HCO$_3^-$/CO$_2$ is much lower than for the Co-Cu/HCO$_3^-$/CO$_2$ system (2.0 mA cm$^{-2}$) prepared under very similar conditions. As the CPE profile for Co-Pi in neutral phosphate solution shows a monotonic decrease in the current density over time and exhibited more stability in the neutral HCO$_3^-$/CO$_2$ system, this leads us to conclude that cobalt-oxide based electrocatalysts are not very stable in phosphate solution, and neutral bicarbonate solutions represent a novel and possibly excellent electrolyte system for electrocatalytic water oxidation assemblies.

There is a clear indication of an increase in the currents for catalyst deposition and catalytic currents for water oxidation reaction as the current density varies linearly with the [Co(II)] in aqueous NaHCO$_3$ electrolyte (Figure 5). After five potential scans, a thick deposit of the Co-Cu based water oxidation catalyst film on ITO was obtained with a high concentration of Co$^{2+}$ in a deoxygenated and CO$_2$ saturated bicarbonate solution (pH $\approx$ 6.7). The oxygen evolution peak current density for a bicarbonate solution with only 0.4 mM Co$^{2+}$ increases from $\approx$2.5 mA cm$^{-2}$ to a $\approx$4.0 mA cm$^{-2}$ with 4.0 mM Co$^{2+}$ concentration. It was recently shown that for a Cu(II)-based electrocatalyst generated on a glassy carbon anode in a 0.1 M NaHCO$_3$ solution saturated with CO$_2$ (1 atm, pH = 6.7), the catalytic current density for water oxidation CV’s between 0.4 V to 1.65 V (vs NHE) varies with Cu(II) concentration to the limit of 1.2 mM solubility of CuSO$_4$ in aqueous NaHCO$_3$. However, in case of Co$^{2+}$ in a CO$_2$ enriched aqueous bicarbonate system, a solubility up to 4.0 mM of the Co$^{2+}$ is attained at similar pH (pH = 6.7) with a remarkable system performance for water oxidation (Figure 4). This shows that the Co$^{2+}$ based system is much more efficient for water oxidation than the electrodeposited Cu(II) type catalyst in neutral HCO$_3^-$/CO$_2$ system.

At 1.65 V (vs NHE) a peak current density of $\approx$0.5 mA cm$^{-2}$ was obtained on a glassy carbon electrode with 1.2 mM CuSO$_4$ in aqueous NaHCO$_3$. However, the oxygen evolution peak current densities are very promising for the Co(II) in CO$_2$ enriched aqueous NaHCO$_3$. With only a 1.0 mM concentration of Co$^{2+}$, the peak current density for O$_2$ generation is $\approx$2.4 mA cm$^{-2}$ on an ITO electrode (Figure 4). An increase of the catalytic efficiency is also observed for the Co-Ci type electrocatalyst for water oxidation that is generated on an ITO electrode from a CO$_2$ saturated solution by raising the bicarbonate concentration. A peak current density of $\approx$4.15 mA cm$^{-2}$ at 1.6 V (vs NHE; pH = 6.7–6.8) is observed with 0.75 M aqueous NaHCO$_3$ and the $J$ increases linearly going from 0.1 M to 0.75 M aqueous bicarbonate. At high concentration, i.e., more than 0.75 M aqueous NaHCO$_3$, the CV behavior changed and the current density was reduced to $\approx$2.15 mA cm$^{-2}$ at 1.6 V (vs NHE; pH = 6.7–6.8). The Co-Cu electro-deposition wave at $\approx$0.95 V–1.29 V (vs NHE) also diminished, indicating a different fate of the electrocatalyst film on ITO (Supporting Information Figure S8). However, oxygen bubbles were observed on the ITO at 1.6 V (vs NHE). It can be inferred that a near-complete coordination of the Co$^{2+}$ species in the CO$_2$ enriched bicarbonate solution could give rise to this behavior. The presence of CO$_2$ in the electrolyte has another important role. It helps in maintaining the pH close to neutral value, thus avoids the precipitation of Co-hydroxide during electrodeposition. In addition, CO$_2$ also makes a complex type structure with Co$^{2+}$ that induces the electrodeposition process in bicarbonate system. During the experiments while varying the bicarbonate concentration in CO$_2$ saturation in the presence of Co$^{2+}$, the pH of the system remained close to neutral. The excess amount of bicarbonate may induce a different fate or complexation of the metal ions with CO$_2$ that results in different behavior of the Co-Ci in a high concentration bicarbonate system.

In conclusion, we have found that a neutral HCO$_3^-$/CO$_2$ electrolyte is a novel and excellent system for in situ formation of a highly robust and efficient water oxidation electrocatalyst.
derived from cobalt(II) under benign conditions. The cobalt-based Co-Ci electrocatalyst is quickly generated on ITO substrate or on a glassy carbon electrode in neutral HCO$_3^-$/CO$_2$ solution, at about 1.2 V (vs NHE). It is noteworthy that the Co-Ci based water oxidation electrocatalytic system presented here is developed in situ in a simple bicarbonate system rather than in proton abstracting phosphate or borate buffers that have been reported to be essential for the electrodeposition and anodic water oxidation.\(^{[21]}\) The oxygen onset is just at 1.29 V (vs NHE) in a near-neutral pH bicarbonate solution, and the oxygen evolution peak current density is more than 4.0 mA cm$^{-2}$ on ITO and approaching 9.0 mA cm$^{-2}$ on a GC disk at just 1.59 V (vs NHE). These numbers are the highest reported to date for a water oxidation electrocatalytic system in a neutral HCO$_3^-$/CO$_2$ electrolyte system. Hence, the replacement of a fluoride (pH = 3.4), phosphate (pH = 7), borate solution (pH = 9.2) with a bicarbonate electrolyte can be effectively employed to make highly efficient electro-driven water oxidation systems derived from readily available cobalt.\(^{[25–27]}\)

Another unique feature of the Co-Ci system is its remarkable activity in clean electrolyte solution without having Co$^{2+}$ present in the system. This is the first instance where a Co-based electrocatalyst shows such tremendous activity and stability (compared to the Co-Pi catalyst) in a Co$^{2+}$-free electrolyte solution. Once the Co-Ci is deposited on the anode, it remains active and stable for long-term electrolysis of water. For the Co-Pi type system, a continuous presence of Co$^{2+}$ is needed in the solution for the re-deposition and catalytic activity, as the Co-Pi has a poor stability and very low catalytic turnover number. The long-term controlled-potential electrolysis data of the Co-Ci in the bicarbonate system shows a remarkable oxygen evolution current density of \(\approx 2.0\) mA cm$^{-2}$, which was maintained for several hours. However, while the Co-Pi system reveals a catalytic degradation in clean neutral phosphate buffer, it remains very stable in the clean neutral HCO$_3^-$/CO$_2$ electrolyte system. Surface loading with 7.5 nmol of the electroactive catalytic species per cm$^2$ of the anode generates about 109 µmol of O$_2$ during long-term constant-potential water electrolysis with online oxygen evolution measurements. This indicates an oxygen generation rate of 0.51 pmol of O$_2$ per second. The catalytic film analyzed by EDX shows the presence of carbon (about 30%) in the catalyst layer and Na contents are just under 10%. This makes Co-Ci altogether a new electrocatalytic material for anodic water oxidation under benign conditions. The next step and the prospective importance and novelty of this work is that this electrocatalytic water splitting system can be combined with a CO$_2$-reduction module in a full electrochemical device to generate liquid fuel (formic acid, methanol etc).\(^{[28,29]}\)

We anticipate that this study will provide a good starting point for the electrogeneration of robust catalytic materials for water splitting.

**Experimental Section**

**Electrochemical Methods:** All the solutions for electrochemical measurements and electrodeposition were prepared in ultrapure water (Millipore MilliQ) and the electrochemical measurements were performed in deoxygenated aqueous solutions at room temperature. CV experiments were conducted in a three electrode configuration pyrex glass cell. The working electrodes (WE) in the CVs and catalytic water electrolysis experiments were a freshly mirror finished polished glassy carbon disc of 5.0 mm diameter, embedded in a Teflon shroud, and ITO coated glass substrates (1 cm × 2.5 cm, exposed surface area 1.0 cm$^2$). The catalytic water electrolysis and oxygen evolution measurements were carried out in a three electrode double junction H-type glass cell where the counter electrode chamber was separated by a very fine porosity glass frit. Platinum wire (thickness: 1 mm), shaped into a spiral, was used as a counter electrode (CE). A silver-silver chloride reference electrode (SSCE: Ag/AgCl/KCl) was applied for the investigations in the neutral and higher pH aqueous solutions. All potentials are referred to normal hydrogen electrode (NHE). CV experiments were performed with an Autolab PGstat10 potentiostat controlled by GPES-4 software.

**Electrodeposition of the Co-Bicarbonate Catalyst Film:** The Co-Ci based electrocatalyst for water oxidation was generated on an ITO electrode or GC disk in situ from a CO$_2$ saturated (1 atm) sodium bicarbonate solution (0.1 M–1.0 M; pH = 6.7–6.8) containing Co$^{2+}$ (0.5 mM–5 mM), during the CVs between 0.0 V–1.3 V (vs NHE). The catalyst film was also generated while holding the potential of the working electrode above 1.2 V (vs NHE). The so-prepared electrocatalytic film of cobalt based catalyst on the ITO or GC substrate was dried in air and directly subjected to experimentations without any delay.

**Co-Ci Catalyst Film Characterization:** Surface morphology and nature of the electrodeposited catalyst films were characterized by SEM, XPS, and EDX. For EDX analysis, an electrocatalyst film of Co-Ci was electrodeposited via CPE at 1.15 V (vs NHE) for 25 min using clean FTO electrode in a CO$_2$ saturated (1 atm) Na-bicarbonate solution (0.1 M) containing 0.1 mM Co$^{2+}$ (pH = 6.7–6.8). The catalyst film generated was rinsed thoroughly with MilliQ water before EDX testing.

**Online Oxygen Measurements:** Oxygen evolution during electrocatalysis was monitored with a calibrated oxygen electrode connected with a digital O$_2$ meter (YSI, Inc., Model 550A). Further oxygen evolution was characterized by online gas chromatography measurements using a micro-gas chromatography system, T-3000 SRI instruments. The gas mixture from the cell was delivered directly to the sampling loop of a gas chromatograph. Sampling points were collected every 10 min, and the gaseous products were analyzed using a packed MolSieve 5A coupled with a thermal conductivity detector (TCD). Ar (99.9999%) was used as the carrier gas during the GC analysis.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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