Investigation of a Cu(core)/CuO(shell) Catalyst for Electrochemical Reduction of CO_2 in Aqueous Soultion

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In this work, we investigate the electrochemical reduction of CO_2 on a Cu(core)/CuO(shell) catalyst in aqueous electrolytes in a flow reactor. This catalyst predominantly produce CO and HCOOH, and Faradaic efficiency are 21.5% and 20.2% at -1.73 V *vs*.Ag/AgCl, respectively. During the process of electrochemical reduction of CO_2 in aqueous solution, a small amount of methanol is produced, Faradaic efficiency is around 1% ~ 2.5%. A study of the electrochemical behavior of Cu(core)/CuO(shell) in a standard three-electrode cell reveal transformations between Cu, Cu(I), and CuO as a function of applied potential. The results are confirmed by XPS. This interplay between different Cu oxidation states and the presence of the oxide surface to promote proton adsorption may benefit the formation of complicated products.

1. INTRODUCTION

Large scale consumption of fossil fuels has increased atmospheric CO_2 levels over the last 100 years to its current, still increasing level of about 400 mg L^{-1}. These high atmospheric CO_2 concentrations have been linked to severe environmental problems such as climate change[1, 2]. New approaches to mitigate carbon output from the use of fossil fuels as well as methods to fully exploit carbon neutral, renewable energy sources are needed. A possible approach to slow down the increase in atmospheric CO_2 levels is to convert CO_2 to value added chemicals such as liquid fuels using renewable-energy sources (solar, wind, tidal, etc.). Such an approach has the potential to establish a carbon neutral energy cycle[3-7]. Furthermore, most renewable energy sources are intermittent, so

methods for large scale energy storage or on-demand utilization need to be developed. Electrochemical reduction of CO_2 can reduce atmospheric CO_2 concentrations and use excess electricity from intermittent renewable energy sources to convert CO_2 to intermediates for chemical productions at scale[3, 4, 8-11].

The electrochemical reduction of CO_2 in aqueous solution has received considerable attention in the past few decades[9, 10]. Most studies to date have focused on metal electrodes and transition metal complexes electrochemical reduction of CO_2, like rubidium, and silver based catalyst[9, 10, 12], which was always noble metals. However, recent reports indicate that copper or copper oxide catalysts can be used for the electrochemical or photo-reduction of CO_2 in aqueous solution[13-15], it seems that electrochemical reduction of CO_2 on a catalyst having a metal core / metal oxide shell structure has not been reported previously. When using Cu-based catalysts, mixtures of potentially interesting chemicals for industrial applications, including CO, HCOOH, HCHO, CH_3OH, as well as short hydrocarbons (mostly C1-C3) are produced[3, 16, 17]. Tuning the selectivity of Cu-based catalyst systems to produce a single product, or a mixture predominantly comprising of the desired product, has been a big challenge. Here, we studied a Cu(core)/CuO(shell) catalyst for the electrochemical reduction of CO_2 in aqueous solution to CO, HCOOH, and / or CH_3OH in a flow reactor, and we explored possible reaction pathways.

2. EXPERIMENTAL SECTIONS

Catalyst inks were prepared by mixing 200 μL Millipore water, 4 mg catalyst (Cu(core)/CuO(shell) nanopowder, Alfa Aesar, APS 20-40 nm, 99.9%, metal basis), 5.2 μL of a 5 wt % Nafion® solution (Fuel Cell Earth), and 200 μL isopropyl alcohol (Fisher scientific, 99.9%). The ink was sonicated (Vibra-Cell ultrasonic processor, Sonics & Materials) for 15 minutes and then hand-painted on the micro porous layer of a Sigracet 35 BC gas diffusion layer (GDL, Ion Power) with a geometric area of 4 cm^2. The anode used in this study had a 1 mg cm^{-2} loading of Pt black (high surface area, Alfa Aesar) on a Sigracet 35BC GDL.

Cyclic voltammetry (CV) experiments were conducted in a standard three-electrode cell equipped with a glassy carbon electrode RDE as the working electrode, a platinum gauze as the counter electrode, and a Ag/AgCl as the reference electrode (RE-5B, BASi), using 1 mol L^{-1} $KHCO_3$ (Sigma Aldrich, 99.7%) as the electrolyte. Catalyst layers for the CV experiments were prepared by dropping 5 μL of catalyst inks on a glassy carbon rotating disk electrode (RDE) and then drying under N_2 flow.

The flow reactor experiments were carried out under ambient conditions in a flow cell reported previously[12]. A Nafion 117 membrane separated the cathode and anode compartments to prevent poisoning of the anode by CO[18]. A potentiostat operating in steady-state chrono-amperometric mode was used to measure the resulting current as previously reported[12]. The individual electrode potentials were measured using multimeters connected to each electrode and a Ag/AgCl reference electrode in the exit stream. CO_2 from a cylinder was introduced at a flow rate of 7 mL min^{-1} in the standard station using a mass flow controller (246C, MKS instrument). A syringe pump (PHD 2000,

Harvard Apparatus) supplied the 1 mol L^{-1} $KHCO_3$ electrolyte at 0.5 mL min^{-1}. The cathode gas products (*i.e.*, CO) was analyzed by gas chromatography. HCOOH was analyzed using ^{1}HNMR (VARIAN UNITY INOVA500 MHz) using 1 mmol L^{-1} dimethylsulfoxide (DMSO, Fisher scientific, 99.9%) as the internal standard, and CH_3OH was detected using GC-MS.

3. RESULTS AND DISCUSSION

3.1 Electrolysis of CO_2 in a flow reactor

The chrono-amperometric electrolysis was carried out in a flow reactor using gas diffusion electrodes. Table 1 summarizes the Faradaic efficiencies of the different detected products: CO, HCOOH and CH_3OH. Other products may have formed as well, but in much smaller quantities. We observed that the Faradaic efficiency of CO and HCOOH gradually increased with increasingly negative potentials applied to the cathode, from less than 10% to about 20%, which was shown more CO_2 was involved the electrochemical reduction reaction on Cu(core)/CuO(shell) catalyst at the negative cathode potential.

Table 1. Current density and product distributions for the electrochemical reduction of CO_2 on Cu(core)/CuO(shell) at different potentials

Cathode potential (V *vs*.Ag/AgCl)	Current Density (mA cm^{-2})	Faradaic Efficiency (%)[a]			
		CO	HCOOH	CH_3OH	Total
-1.18	5.7	7.5	-	-	7.5
-1.35	17.3	10.4	9.7	2.5	22.6
-1.46	29.2	12.3	15.8	2.0	30.1
-1.59	40.5	15.9	20.0	1.2	37.1
-1.73	54.6	21.5	20.2	1.0	42.7
[a] The error in reported Faradaic Efficiency value is ±0.2%.					

In this study, using Cu(core)/CuO(shell) as the catalyst, Faradaic efficiency of CO was 21.5% at -1.73 V *vs*.Ag/AgCl, which was more positive potential than those reported previously. However, previous report show Faradaic efficiency was up to 80%, the noble metals were used as catalyst in 0.1 mol L^{-1} $KHCO_3$[19]; and Azuma *et al* electrochemical reduction of CO_2 to CO at -2.0 V *vs*.SCE (so -2.035 V *vs*.Ag/AgCl) using Pd wire as electrode, Faradaic efficiency of CO was 12%[20].

Faradaic efficiency of HCOOH was 20.2% at -1.73 V *vs*.Ag/AgCl. Ryu *et al* electrocatalytic of CO_2 to HCOOH in neutral solution using Hg[21], Faradaic efficiency was nearly 100%, but Hg was not used any more for the environmental problem. Using copper as electrode, Faradaic efficiency of HCOOH was 9.4% at -1.44 V *vs*.NHE (so -2.051 V *vs*.Ag/AgCl)[19]. Current density from 5.7 to 54.6 mA cm^{-2} was simultaneously higher than those reported (0~10 mA cm^{-2})[19, 21]. Those experimental

results observed that this catalyst (Cu(core) / CuO(shell)) has special effect on electroreduction of CO_2 in aqueous solution.

A small amount of the most desirable product, CH_3OH, could also be detected. The Faradaic efficiency of CH_3OH decreased from a maximum of 2.5% to about 1% with increasingly negative cathode potentials (from -1.35 to -1.73 V *vs.*Ag/AgCl). Faradaic efficiency for methanol (1-2.5%) is about ten times higher compared to previous reports that used Cu foil as the cathode catalyst (0.2 % at -1.14 V *vs.*RHE (so –1.751 V *vs* Ag/AgCl) in 0.1 mol L^{-1} $KHCO_3$)[16].

Generally speaking, the greater production in our study may be due to the electronic structure of the core/shell Cu/CuO catalyst and the promoting effect of Cu(I) species produced from the reduction of CuO. For example, the catalyst may undergo a transition of CuO(shell) to Cu(I) and Cu(I) to Cu(core) during the electrochemical reduction process, in which the generated Cu(I) can promote the reduction of CO_2. The more negative cathode potential, the higher total Faradaic efficiency of CO, HCOOH and CH_3OH was. Based on the experimental result, much proton in aqueous solution reacted with CO_2 at negative potential on the Cu(core)/CuO(shell) catalyst during the process of electrochemical reduction.
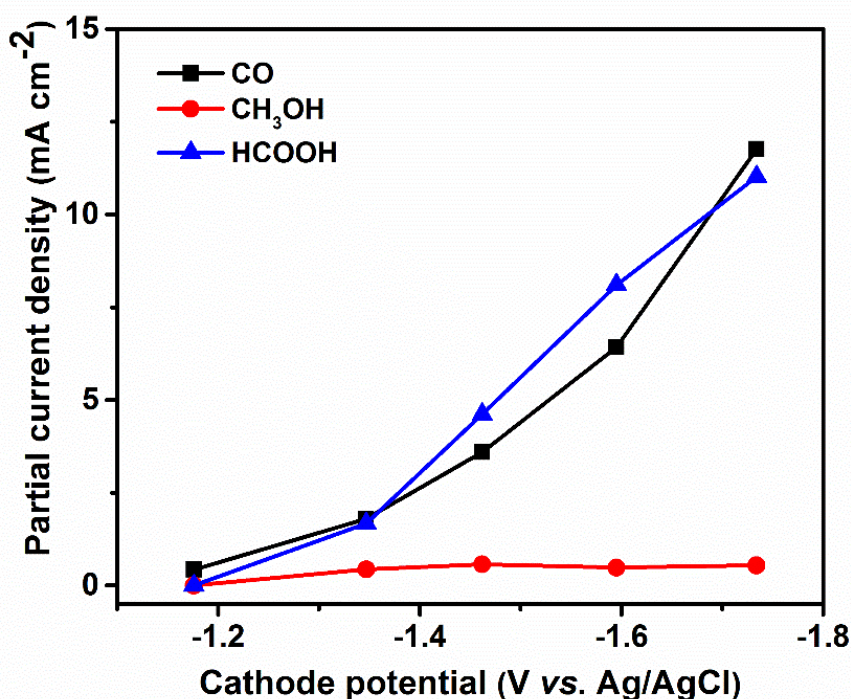

Figure 1. Partial current density for different products as a function of cathode potential (experiments performed at room temperature and ambient pressure in 1 mol L^{-1} $KHCO_3$).

The partial current density for the different products as a function of cathode potential was shown in Figure1. With increasing cathode potentials, the partial current densities for CO and HCOOH increased, while a slight decrease could be observed for the current density of methanol. Table 1 also indicates that the catalyst more selectively produces CO and HCOOH than methanol,

which is relative to the electrocatalytic property of copper[22] for electrochemical reduction of CO_2 in aqueous solution.

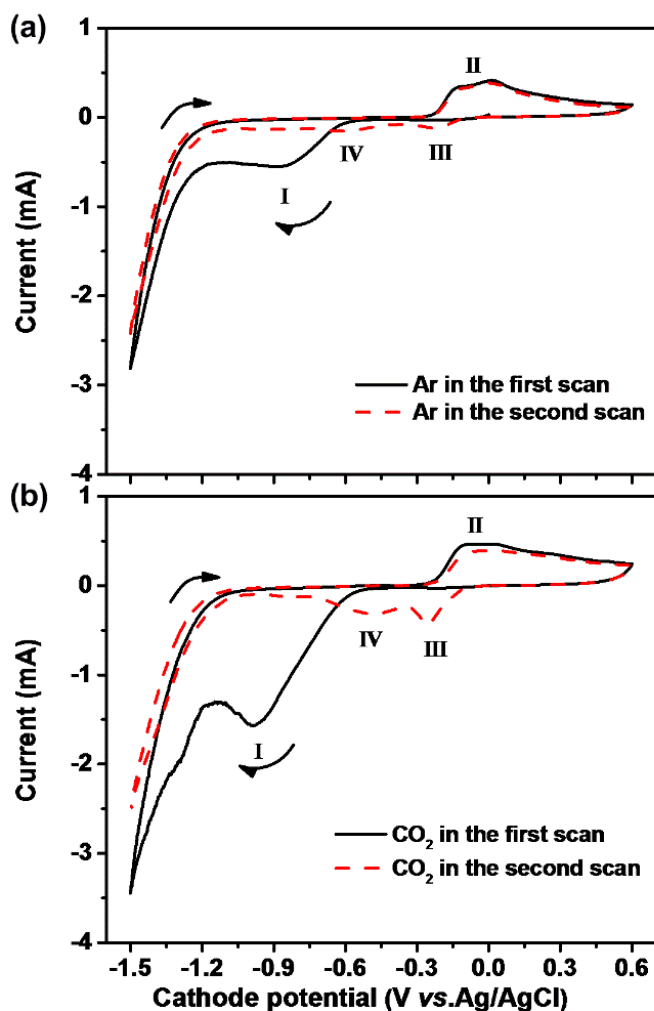*3.2 Electrochemical behavior of Cu(core)/CuO(shell) catalyst*

Figure 2. Cyclic voltammograms when using Cu(core)/CuO(shell) as the cathode catalyst measured after bubbling Ar (a) and CO_2 (b), respectively. The experiment was conducted in 1 mol L^{-1} $KHCO_3$ at a scan rate of 0.1 V s^{-1}.

In our study, we successfully observed the formation of CO, HCOOH and CH_3OH using 1 mol L^{-1} $KHCO_3$ in a flow reactor.   Therefore we studied the electrochemical behavior of the Cu(core)/CuO(shell) catalyst in detail using cyclic voltammetry. As evident from Figure 2a and 2b, the voltammogram measured when the electrolyte is saturated with CO_2 is different from the voltammogram measured after saturation with Ar. The peak current was much higher in the presence of CO_2. In the first scan, a reductive peak around -0.87 V (peak I in Figure 2a) was observed after bubbling Ar. In the reverse scan two small successive oxidative peaks appeared at -0.12 V and -0.01 V

(II in Figure 2a), respectively. These two peaks were also present in the second scan. The two oxidative peaks correspond to the oxidation of Cu to Cu(I) and Cu(I) to CuO, respectively, which is in agreement with prior work[23]. In the second scan, two reductive peaks were observed at -0.22 V and -0.62 V (III and IV in Figure 2a), which can be attributed to the transition of CuO to Cu(I) and Cu(I) to Cu, respectively. The peak I in the first scan disappeared in the second scan. At negative potentials, the CuO(shell) might be reduced to Cu. Therefore, we attributed the reductive peak in the 1st scan to the combination of the reduction of CuO(shell) to Cu(I) and Cu. After the majority of the CuO(shell) was converted to Cu(I) and Cu, the structure of the catalyst changed to a more stable structure. Therefore any scan after the 1st scan had similar reductive peaks. Only the 2nd scan is shown in Figure 2a and 2b, but subsequent scans were similar to the 2nd scan. However, when the 1 mol L^{-1} KHCO$_3$ solution was saturated with CO$_2$, some of the peaks shifted and the current increased significantly, which may be due to the reduction of CO$_2$ on the catalyst surface.
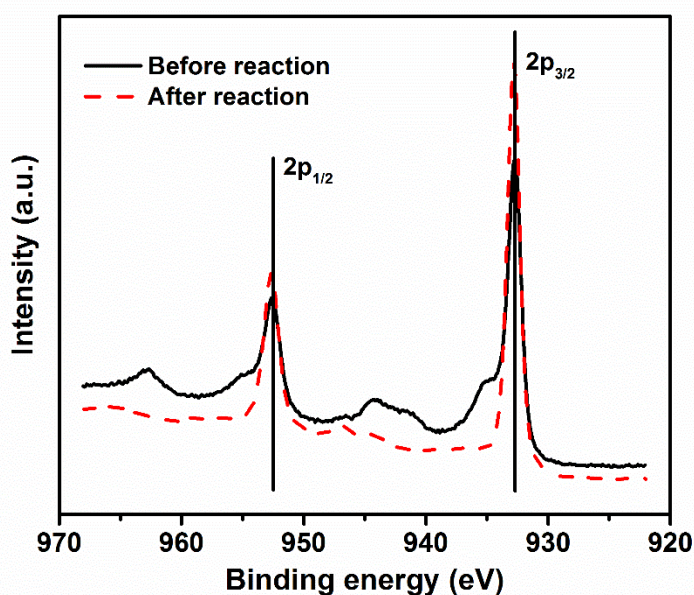
3.3 XPS analysis of the Cu(core)/CuO(shell) catalyst

Figure 3. XPS spectra for Cu(core)/CuO(shell) catalyst, analyzed before and after electrochemical reduction of CO$_2$.

We used X-Ray Photoelectron Spectroscopy (XPS) to characterize the cathode catalyst before and after the reaction, which were shown in Figure 3. In the Cu(core)/CuO(shell) catalyst, copper oxide usually exists in the divalent state. In the catalyst samples before being exposed to electrochemical reaction, two satellite peaks were observed at 934.9 eV and 944.2 eV, which indicates the presence of Cu(II)[24]. In addition, two prominent peaks can be observed at 932.5 eV and 952.7 eV, presumably corresponding to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$, respectively. Both peaks are the characteristic of Cu or Cu(I); the Cu 2p$_{3/2}$ and 2p$_{1/2}$ peaks for Cu and Cu (I) overlap[25]. After exposing the catalyst to electrochemical reaction, the two peaks indicating the presence of Cu(II) were significantly smaller,

while the two peaks at 932.5 eV and 952.7 eV both had increased. These changes suggest that the conversion of the CuO(shell) to Cu(I) and to Cu(core) takes place during the electrochemical reduction process. These observations confirm our interpretation of the presence of Cu(I) in the cyclic voltammogram reduction scan of the Cu(core)/CuO(shell) catalyst. However, we could not confirm the presence of Cu(I) with XPS, because Cu(I) and Cu have similar characteristic peaks in XPS[25].

3.4 Reaction pathway

Based on our experimental results as well as reaction mechanisms reported previously[14, 26, 27], we propose a potential reaction pathway for the electrochemical reduction of CO_2 using a Cu(core)/CuO(shell) cathode catalyst (Scheme 1). The first step in the electrochemical reduction of CO_2 is a one electron transfer to form $CO_2^{\bullet-}{}_{ads}$ on the surface of cathode catalyst, then $CO_2^{\bullet-}{}_{ads}$ further reacts to form CO_{ads} or formate, the latter being a dead-end in the reaction pathway, leading to HCOOH as the product. The CO_{ads} can be released to form CO as a product, but for many other products CO_{ads} is the starting point. Literature suggests that the adsorption of CO is accompanied by proton adsorption, which can result in the formation of a surface formyl (HCO) species[26]. Once the HCO species is formed, further protonation and electron transfer reactions can lead to the formation of CH_4, or alternatively the CH_3O adsorbate is formed. The surface of the Cu(core)/CuO(shell) may thus promote the addition of hydrogen to the oxygen atom of the CH_3O adsorbate, resulting in the formation of the most desired product CH_3OH. But electrochemical reduction of CO_2 on Cu(core)/CuO(shell) catalyst was carried out in a flow reactor, which caused the adsorbed radical form CO and HCOOH easily.
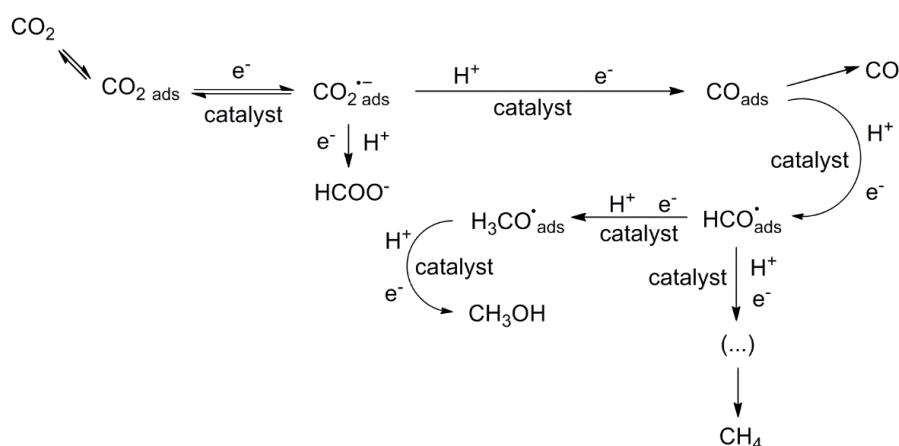
Scheme 1. Possible reaction pathway for the electrochemical reduction of CO_2 on Cu(core)/CuO(shell) catalyst.

4. CONCLUSION

In this study, we investigated the electrochemical reduction of CO_2 using a Cu(core)/CuO(shell) catalyst in a flow reactor, and it was found that a mixture of three or four

products (CO, HCOOH, CH$_3$OH and H$_2$) in different relative and absolute amounts was formed, depending on the cathode potential. Faradaic efficiency of CO and HCOOH were higher than those reported previously, 21.5% and 20.2%, respectively. Interestingly, a larger amount of CH$_3$OH, a highly desirable product to be obtained from CO$_2$ reduction, was obtained with the Cu(core)/CuO(shell) catalyst than what has been reported previously for Cu foil-based catalysts. At -1.73 V *vs*.Ag/AgCl potential, total Faradaic efficiency was 42.7%. A study of the electrochemical behavior of the Cu(core)/CuO(shell) catalyst in 1 mol L^{-1} KHCO$_3$ as the electrolyte using a 3-electrode cell revealed that the Cu catalyst transformed between various oxidation states of copper, namely copper oxide (CuO), and Cu(I), and copper metal (Cu). This observation was further supported by XPS data of the catalyst before and after use in electroreduction of CO$_2$. Based on our experimental data, we proposed a reaction pathway for the electrochemical reduction of CO$_2$ which is meant to guide further development of cathode catalyst that are more selective for individual products, especially methanol. Our results suggest that the interplay between the Cu core and CuO shell is beneficial for the production of CO, HCOOH and methanol, but the catalyst needs to be modified further to suppress the pathways leading to other products such as H$_2$ during the process of electrochemical reduction of CO$_2$.

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