Journal of Electroanalytical Chemistry 716 (2014) 53–57

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

The influence of pH on the reduction of CO and CO_2 to hydrocarbons on copper electrodes

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ARTICLE INFO

Article history:
Available online 11 September 2013

Dedicated to Professor Kingo Itaya on the occasion of his 65th birthday and in recognition of his seminal contributions to physical electrochemistry

Keywords:
Carbon dioxide
Electrochemical reduction
Copper single crystal electrodes
pH dependence
Reaction mechanism
Carbon monoxide

ABSTRACT

The pH is an important parameter in the reaction mechanism of the electrochemical reduction of carbon dioxide and carbon monoxide to methane and ethylene on copper electrodes. We have investigated the influence of the pH on this reaction using Cu(111) and Cu(100) single crystal electrodes. The results support our recently proposed reaction mechanism, in which two different reaction pathways to ethylene can be distinguished: a first, pH-dependent pathway that has a common intermediate with the formation of methane that occurs mainly on Cu(111), and a second, pH-independent pathway *via* a carbon monoxide dimer. The latter pathway occurs on Cu(100) only.

1. Introduction

The still increasing global CO_2 emissions are causing widespread concerns about the possible consequences. Mimicking photosynthesis, by reducing carbon dioxide to hydrocarbons, could be an important step forward in the reduction of carbon dioxide emissions. In this respect, an important discovery was done by Hori in the 1980s, who showed that CO_2 can be electrochemically reduced to hydrocarbons on copper electrodes [1]. Only copper electrodes have been found to catalyze this reaction to a significant extent, and the main carbon products are methane and ethylene [2]. This process could be a solution to store (surplus) sustainable electrical energy as chemical energy, that could be directly used in the current fuel (e.g. natural gas) infrastructure.

Since its discovery, ample research has been performed to understand the molecular mechanism of this reaction [3–9], and to relate the product selectivity to the electrode surface structure [4,5,10–15]. A better understanding of this reaction on the molecular level could lead to an improved product efficiency and selectivity.

One important parameter in this reaction is the pH. Hori has shown that the formation of methane depends on pH, whereas the formation of ethylene is independent of pH [3]. This observation has played an important role in the various proposed molecular mechanisms [3,5,9]. Therefore, we investigate in this paper the influence of pH on the reduction of CO and CO_2 on Cu(100) and Cu(111). We used these electrodes because we have shown in previous work that there are two different reaction pathways from CO to ethylene [12,16]: a first pathway that has a common intermediate with the formation of methane and that takes place both at Cu(111) and Cu(100) surfaces, and a second pathway in which CO is selectively reduced to C_2H_4 at relatively low overpotentials, presumably through the formation of a surface adsorbed CO dimer. The latter pathway takes place preferentially at (100) facets, and we expect this reaction pathway to be independent of pH. We have studied the pH dependence both in phosphate buffers and in electrolytes with non-specifically adsorbing anions, using online electrochemical mass spectrometry (OLEMS) [17]. This technique allows us to follow the formation of products while changing the potential at the electrode. In this way, we can measure the onset potentials for the different products as a function of pH, and investigate the pH dependence for the different products formed.

2. Experimental

All experiments were carried out in an electrochemical cell using a three-electrode assembly at room temperature. The cell and glassware were boiled in ultra clean water (Millipore MilliQ gradient A10 system, 18.2 MΩ cm) before each experiment. A gold

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http://dx.doi.org/10.1016/j.jelechem.2013.08.033

wire was used as counter electrode and a reversible hydrogen electrode (RHE) in the same electrolyte was used as reference electrode. All potentials in this paper are referred to this electrode. The potential was controlled using an Ivium A06075 potentiostat.

The single crystal copper electrodes used were bead-type electrodes (icryst) cut and polished with an accuracy down to 0.5°. Prior to each experiment the electrode was electropolished in 66% H_3PO_4 at 3 V vs. a Cu counter electrode for 10 s [18]. After polishing, the surface quality was verified regularly using blank voltammetry in 0.1 M NaOH [19].

The experiments were carried out in 0.2 M phosphate buffers, 0.2 M $NaClO_4$ solutions or 0.1 M $HClO_4$, H_3PO_4 or NaOH, all prepared from high purity reagents (Sigma–Aldrich TraceSelect, Merck Suprapur) and ultra clean water. Argon (Air Products, 5.0) bubbling was used to deaerate the electrolyte, before saturation of the electrolyte with carbon monoxide (Linde, 4.7) or carbon dioxide (Linde, 4.5).

Online electrochemical mass spectrometry (OLEMS) was used to detect the gaseous products formed during the reaction [17]. The reaction products at the electrode interface were collected with a small tip positioned close (~50 μm) to the electrode.The tip is a 0.5 mm diameter porous Teflon cylinder with an average pore size of 10–14 μm in a Kel-F holder. This tip is connected to a mass spectrometer with a PEEK capillary. The tip configurations were cleaned in a solution of 0.2 M $K_2Cr_2O_7$ in 2 M H_2SO_4 and rinsed with ultra pure water before use. A SEM voltage of 2400 V was used, except for hydrogen ($m/z = 2$) where a SEM voltage of 1200 V was used. The products were measured while changing the potential of the electrode from 0.0 V to −1.0 V or −1.5 V with 1 mV s^{-1}. Because the equilibration of the pressure in the system after introduction of the tip in the electrolyte takes a very long time, all mass fragments show a small decay during the measurement. We corrected for this background by fitting a double exponential function to the data in the potential regions were no change in activity is observed and subtracted this fit from the data. All mass fragments shown in this paper have been background corrected in this way. In order to compare and present the various mass fragments in one graph, all mass fragments have been normalized, which is done by dividing each signal by its highest value.

3. Results

Fig. 1 shows the gaseous products of CO reduction in 0.1 M phosphoric acid (pH 1) and 0.2 M phosphate buffers (pH 7 and 12) on Cu(1 1 1) and Cu(1 0 0), measured with OLEMS. The three detected products are hydrogen ($m/z = 2$), methane (represented by $m/z = 15$) and ethylene (represented by $m/z = 26$). By comparing these three different products, it is clear that they have a different potential dependence. Both on Cu(1 1 1) and Cu(1 0 0), hydrogen formation always starts around −0.35 V, increasing with more negative potentials. Interestingly, at pH 12, the hydrogen formation is limited till −0.9 V, after which it rapidly increases. The formation of methane shows some differences between Cu(1 1 1) and Cu(1 0 0) at the various pH values. At pH 1, the formation of methane is earlier on Cu(1 0 0), starting at −0.45 V. At pH 7, the formation of methane is similar on Cu(1 1 1) and Cu(1 0 0), starting at around −0.85 V. At pH 12, the formation of methane is quite similar on Cu(1 1 1) and Cu(1 0 0), starting a little earlier on Cu(1 1 1). The biggest differences are observed for the ethylene formation. At pH 1, there is only a very small fraction of ethylene observed on Cu(1 0 0). At pH 7 and 12, the formation of ethylene is much earlier on Cu(1 0 0) compared to Cu(1 1 1), and starts at around −0.4 V.

Similar experiments were performed in electrolytes with non-specifically adsorbing anions, the results of which are shown in Fig. 2. We have used 0.1 M $HClO_4$ (pH 1), 0.01 M $HClO_4$ + 0.19 M $NaClO_4$ (pH 2), 0.2 M $NaClO_4$ (pH 7) and 0.1 M NaOH (pH 13). Since at some pH values products were only observed below −1.0 V, we have scanned the potential till −1.5 V. The onset of the hydrogen formation in these electrolytes is similar compared to the phosphate-based electrolytes. Again, the formation of methane is earlier on Cu(1 0 0) at pH 1. Also, ethylene is not observed at pH 1. Ethylene is mainly observed on Cu(1 0 0), and the onset potential clearly shifts with pH, from −0.80 V at pH 2 to −0.30 V at pH 13. Overall, the observed potential dependence is similar in Figs. 1 and 2.

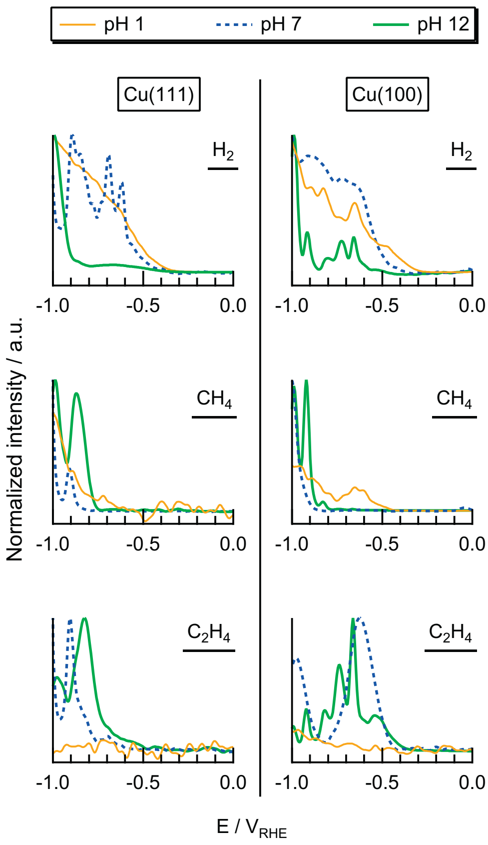

Fig. 1. The reduction of CO in 0.1 M phosphoric acid (pH 1) and 0.2 M phosphate buffers (pH 7 and 12) on Cu(1 1 1) (left) and Cu(1 0 0) (right). With OLEMS, the formation of *H2*($m/z = 2$, top), CH_4 ($m/z = 15$, middle), and C_2H_4 ($m/z = 26$, bottom) were followed.

The onset potentials for the measurements shown in Figs. 1 and 2 are summarized in Table 1. From this table it can be seen again that the formation of methane starts, independent of pH, on average around −0.9 V, with Cu(1 0 0) at pH 1 as a notable exception. The formation of ethylene on Cu(1 0 0) clearly depends on pH, and shifts to less negative potentials with increasing pH.

In Table 1, no values are given for the measurement in a phosphate buffer at pH 2. The reason for that is shown in Fig. 3. In the first reduction cycle, the onset potential both for methane and ethylene is at −1.15 V. In the reverse scan, the hydrocarbon formation continues till 0.6 V (methane) or −0.4 V (ethylene). In the second scan, the onset potential for both methane and ethylene is around −0.5 V. Fig. 3 shows the results for Cu(1 1 1) only, but the same phenomena was observed on Cu(1 0 0) (data not shown). This strong shift in onset potential was only observed for a phosphate buffer of pH 2.

Next to the reduction of CO, we have also investigated the reduction of CO_2. We have only studied the pH dependence of CO_2 reduction in phosphate buffers, since CO_2 itself strongly influences the pH of the unbuffered electrolytes. We could not use the