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Catalytic Activity of Cu and Cu/Sn Electrodes during CO_2 Reduction from Aqueous Media

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In this work, we investigated the catalytic activity of copper-based electrodes during CO_2 reduction from $KHCO_3$ aqueous solutions. Copper electrodes, synthetized by the electrochemical reduction of thermally formed copper oxide (CuRE), or by decorating of CuRE with tin (CuRE/Sn) were tested. Moreover, commercial copper or tin foils have been used for comparison. Different electrochemical techniques such as cyclic voltammeteries and linear sweep voltammetries were adopted in order to derive information on the reductive processes and to characterise the behaviour of the electrodes. Higher cathodic currents were obtained using CuRE and CuRE/Sn with respect to commercial foils. Depending on the applied potential, lower faradic efficiency (FE) is obtained at CuRE/Sn rather than at CuRE, and a very high loading of Sn seems to be required to increase the FE by some percentage points. Interestingly, at the lowest investigated potential (-0.8 V), the presence of Sn, even at low amount, was able to catalyse the formic acid formation, with a FE of 14%.

1. Introduction

Carbon dioxide increases continuously in the atmosphere, due to the growth of anthropogenic emissions, and this has made it an issue of global concern, as CO_2 is considered one of the main greenhouse gases responsible for global warming. In recent years, considerable attention has been paid to the control of CO_2 emissions, and their conversion, in order to mitigate the negative impact of this gas on the atmosphere.
Currently, the emission of CO_2 into the atmosphere can be reduced by several technologies, such as CO_2 capture and storage (Hossain and De Lasa, 2008). A better approach is to convert carbon dioxide into useful liquid fuels and value-added chemicals, such as formic acid, methanol, methane, etc. (Kortlever et al., 2015). Several techniques have been investigated in recent years, such as photochemistry, thermochemistry and electrochemistry, to reduce catalytically CO_2 to fuels and chemicals (Centi et al., 2013; Lim et al., 2014). Among these, the electrochemical approach has become attractive because it has several advantages, such as easy control and scale-up of the process, mild conditions for the electroreduction of CO_2.
The main drawbacks of the electrochemical reduction of CO_2 under ambient conditions include the very negative potential required and the difficulty in controlling the selectivity of the reaction; in fact, the reduction of CO_2 can occur via 2, 6, 8 and 12 electrons, resulting in a variety of products, such as carbon monoxide, formic acid, methanol, formaldehyde, methane and acetic acid. (Hori et al., 2002; Wang et al., 2015; Chen et al., 2015; Merino-Garcia et al., 2017). Among them, formic acid is one of the most interesting due to its highest value-added with respect to the other possible products from CO_2 reduction. Moreover, formic acid is the simplest naturally existing carboxylic acid, and its demand is dramatically expanding, year by year, due to its various applications. For example, a significant proportion of formic acid is used in agriculture as a preservative, due to its natural antibacterial properties. In industry, formic acid is commonly used in the production of leather, the manufacture of rubber and dyeing of textiles, since, unlike mineral acids, it evaporates without leaving any residues. Furthermore, formic acid has been proposed as a feed for fuel cells (Yu and Pickup, 2008).

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However, the steps involved in the reductive processes can proceed very slowly, even when catalysts are used. In addition, the products of electroreduction are commonly a mixture, rather than a single product. Moreover, when the reaction is performed in aqueous solution, the hydrogen evolution reaction (HER) takes place in the same potential range of CO_2 reduction, thus lowering the faradic efficiency (FE) of the process and the selectivity towards a specific product (Lan et al., 2014). In this context, it is advisable to develop new active electrocatalysts that promote the carbon dioxide reduction, suppressing the competing HER. Cu, Bi, Sn and Co show a good level of catalytic activity to hydrocarbons, alcohols, carbon monoxide and formic acid (Hori et al., 1994; Wang et al., 2016; Raciti et al., 2015; Sarfraz et al., 2016; Gao et al., 2016; Hara et al., 1995). Of note Sn, Pb, In, Hg and Cu are indicated as good catalysts for CO_2 electroreduction to formic acid/formate, given that Sn is one of the most electroactive. However, the reaction mechanism is still not well understood, and many issues need to be resolved. The coupling of different substrates could be a better option to obtain higher performance, in terms of both electro-activity and selectivity towards the desired product.

This work aims to give a contribution in this direction, by investigating the behaviour of Cu based electrodes during CO_2 electroreduction from $KHCO_3$ aqueous solution. In particular, starting from a commercial Cu foil, a nanometric structure of copper oxides with high surface area was prepared: the substrate was thermally oxidized and then reduced electrochemically and a decoration of Sn was added to implement the selectivity to formic acid. This synthesis procedure was demonstrated to be effective starting from 3D nanostructured materials (foams (Wang et al., 2016) and mesh (Raciti et al., 2015)) but, to the best of our knowledge, this is the first time that this technique has been applied to a flat 2D commercial foil.

The activity of the samples has been characterized by voltammetric analysis, while the FE for the production of formic acid during galvanostatic electrolysis was evaluated. Cyclic voltammograms and linear sweep voltammograms were recorded to investigate on the redox behaviour of the catalyst in both N_2-saturated $KHCO_3$ (N2-SS) and CO_2-saturated $KHCO_3$ (CO2-SS) solutions. In addition, the production of HCOOH obtained on the synthesized samples, as well as the FE were investigated at different applied potential values.

2. Experimental

All the electrochemical runs were performed in a three-electrode electrochemical cell using a platinum grid and a SCE as counter and reference electrodes, respectively. The electrodes were connected to a potentiostat-galvanostat (Metrhom Autolab 302N, Metrohm Switzerland), controlled by NOVA software.

$KHCO_3$, $SnSO_4$, NaOH, copper foil (99.98%, 0.25 mm thick) and tin foil (99.99%, 0.5 mm thick) were purchased from Aldrich. All chemicals were used without further purification. Before use, the copper foils and tin foils were sonicated in acetone for 10 minutes and then dried under a stream of nitrogen. One side of the electrodes was exposed to the electrolytic bath with 1 cm^2 of nominal area.

The copper oxide-based electrodes (CuRE in the rest of the text) were obtained by annealing a Cu foil in air at 600°C for 8h. The as-grown grain-like structures were reduced to Cu by applying a negative potential at -0.8 V vs SCE for 1h in $KHCO_3$ (0.1M) (Raciti et al., 2015). Moreover, Cu/Sn electrodes (CuRE/Sn in the rest of the text) were also prepared in which Sn was electrodeposited on the copper oxide-based electrodes. The deposition bath was constituted by 2 M NaOH aqueous solution containing 0.05 M $SnSO_4$. A preliminary voltammetric study was performed to identify the potential for the reduction of Sn, which was at -1.4 V. Electrodeposition of Sn was carried out using a pulse potential technique; the potential was switched 15 times between open circuit potential (OCP) and -1.4 V for 5 seconds.

SEM-EDX analyses were performed for the morphological characterisation of CuRE and CuRE/Sn electrodes.

Cyclic voltammograms (CVs) and linear sweep voltammogramms (LSVs) started from OCP in the negative direction at different scan rates in $KHCO_3$ (0.1 M) after bubbling the electrolyte for at least 15 minutes with N_2; the same experiments were repeated saturating the solution with CO_2. CVs were recorded in the potential window between -2 V and 0.5 V (vs SCE) at 50 mV/s, while LSVs were recorded from OCP to -2 V at 1 mV/s. Potentiostatic experiments were carried out at a fixed value of potential for 6 h, and during the experiments CO_2 was continuously bubbled in the solution, which was also magnetically stirred.

Quantitative analysis of the liquid products was carried out at the end of electrolysis tests to investigate the FE and the concentration of the obtained products. The samples were analysed by HPLC (Waters) equipped UV-vis detector. The column was a Omnispher 5 C18 and 0.1 % H_3PO_4 was used for elution at flow rate of 1 mL/min. The detection wavelength was 220 nm.

3. Results and discussion

In Figure 1 SEM analyses of synthesized samples are compared with that of the Cu foil sample at which a thermal oxide layer was obtained. Annealed Cu foil shows non-uniform surface fractures (Figure 1a), while,

after the electrochemical reduction, the microstructure reveals a polycrystalline nature, with aggregated crystals of tetragonal shape (CuRE sample Figure 1b). Further quantitative analyses indicated that the resulting surface at this sample is 90% composed of Cu, while 10% was equally distributed into Cu(I) and Cu(II) oxides. Figure 1c, shows the surface morphology of CuRE/Sn sample at which Sn particles, like dendrites, were deposited. The Sn peaks appear in the EDX spectrum of this sample, confirming that Sn has been successfully electrodeposited on Cu surface (Figure 1d).

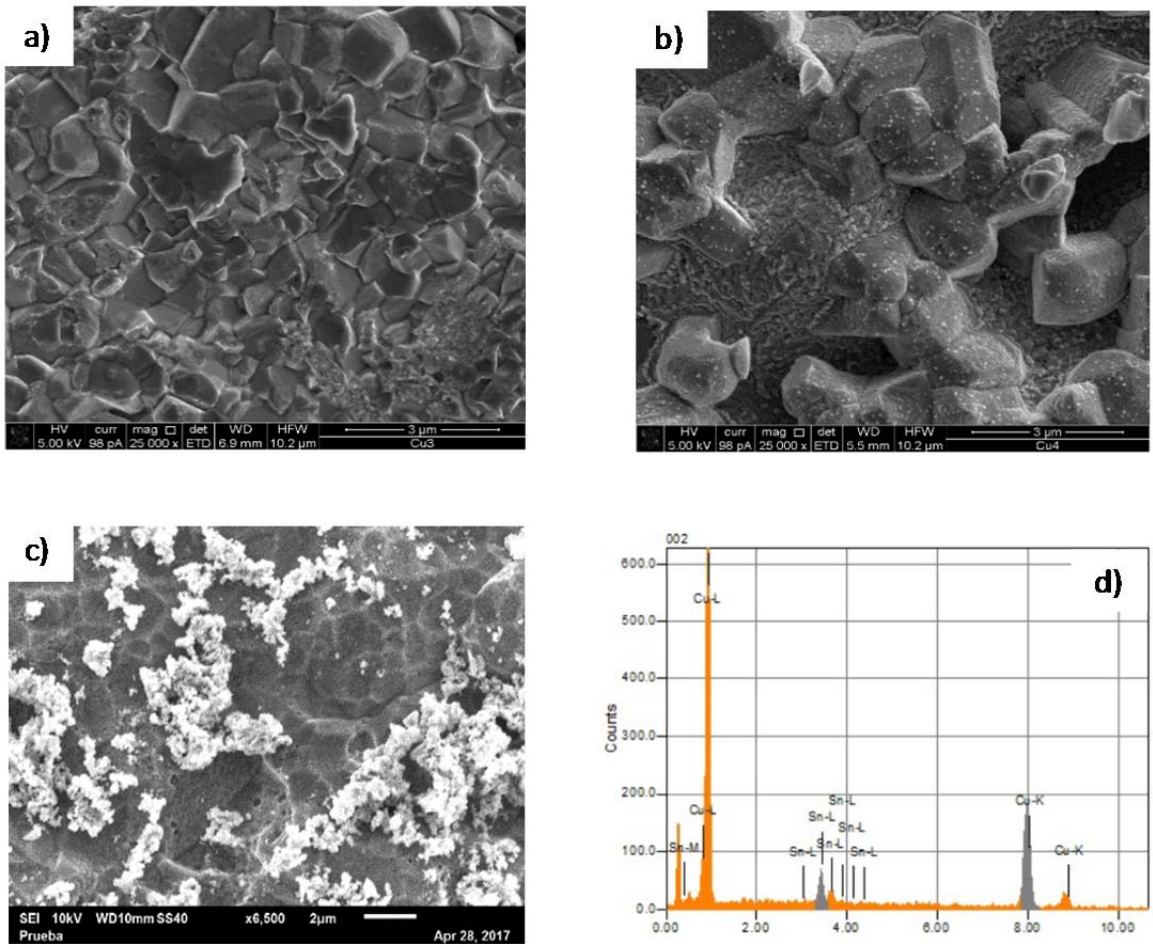

Figure 1 SEM images of: a) annealed Cu foil; b) CuRE; c) CuRE/Sn; and EDX of CuRE/Sn (d).

3.1 Voltammetric behaviour

The electrochemical behaviour of the samples was studied firstly by cyclic voltammetries. In order to better highlight the effect of the CO_2 in the electrolyte, Figure 2 compares, for each electrode, the CV curves obtained in N2-SS and CO2-SS. Moreover, due to the strong influence of pH on the potential at which CO_2 reduction and H_2 evolution occur, as it was suggested by the literature, the potential scale was shifted, accordingly to the difference of pH for the two solutions (Schouten et al., 2014). In fact, the pH value passed from 9.3 in N2-SS, to 6.7 in CO2-SS. Thus, in Figure 2 the CVs are plotted by converting the reference scale using E = E' + 0.0591 V x pH.

As can be observed, a different effect of CO_2 is registered: on Sn foil, only a decrease of the peak current is observed in the presence of CO_2, while neither new peaks, nor a shift in their potential is observed. On the contrary, at Cu based samples the presence of CO_2 leads to a variation of the redox peaks of the surface oxides and, especially at CuRE and CuRE/Sn, it affects the reduction currents in the range of H_2 evolution potential. In all cases, the total current recorded at higher cathodic overpotential in CO2-SS was lower than that obtained at the same potential in N2-SS.

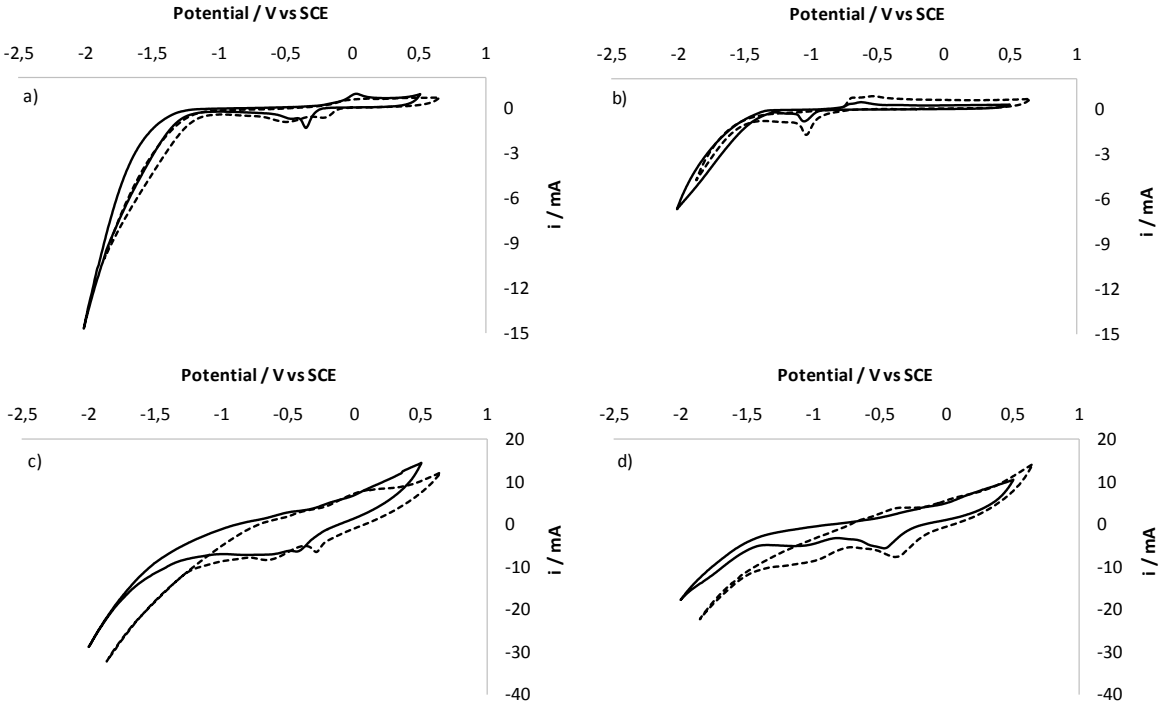

Figure 2 Cyclic voltammograms at: a) Cu foil, b) Sn foil, c) CuRE and d) CuRE/Sn in N2-SS (dashed line) and CO2-SS (solid line). Potential scan rate: 50 mV/s. Curves in N2-SS have been shifted in the potential scale in order to take into account for the different pH.

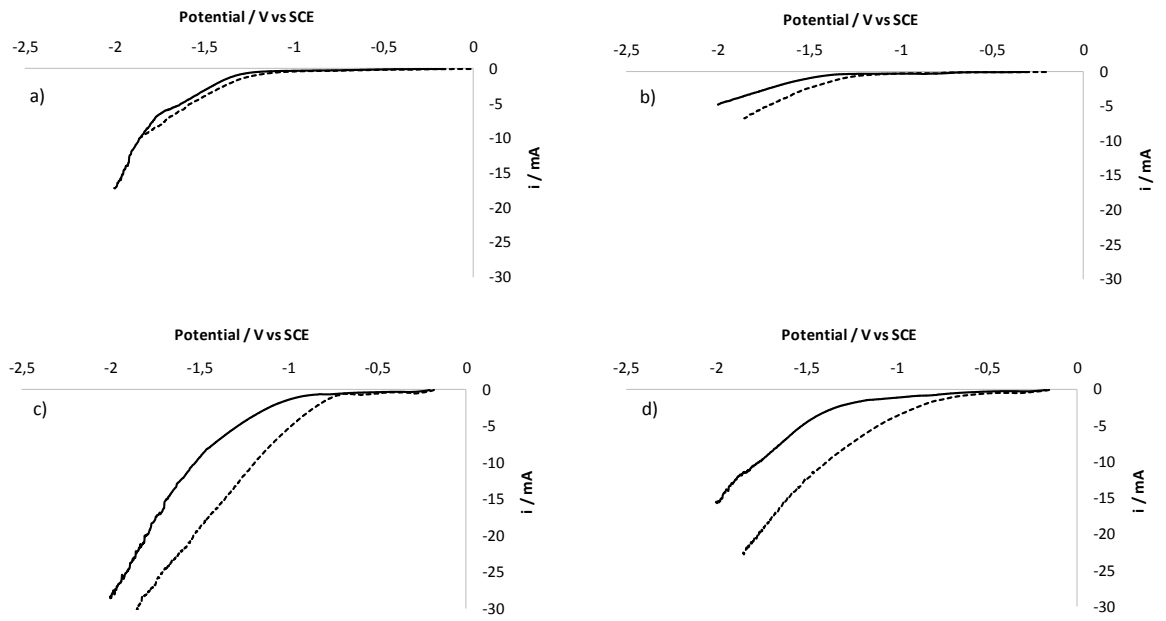

Figure 3 Quasi-steady linear sweep curves obtained on Cu foil (a), Sn foil (b), CuRE (c) and (d) CuRE/Sn, in N2-SS (dashed lines) and CO2-SS (solid lines). Potential scan rate: 1 mV/s. Curves in N2-SS were shifted in the potential scale in order to take account of the different pH.

The trials in quasi-steady-state (Figure 3) confirm these results: also in this case, if compared with commercial electrodes, the synthesized ones show a higher current at all the overpotentials, but also they exhibit a high negative effect of CO_2 on the total current recorded.

This behaviour is in line with that reported in several papers in the literature, on the electroreduction of CO_2 in aqueous electrolytes, at Cu based electrodes. The decrease of current is generally attributed to the possible CO formed as an intermediate specie (Hori et al., 1991): the adsorption of CO suppresses cathodic hydrogen formation thereby favouring the electroreduction of CO_2.

3.2 Potentiostatic electrolysis

Table 1 summarises the results of potentiostatic electrolyses performed at the three potential values of interest, with the synthesized samples. In particular, as detailed in the experimental section, the runs were protracted up to six hours, during which CO_2 was continuously bubbled in the solution.
Analysis of the liquid phase at the end of the runs, revealed different amounts of formic acid and traces of oxalic acid, as a result of the CO_2 reduction. Table 1 summarises the data for the concentration of formic acid, as well as the faradic efficiency for its production.

Table 1: Concentration and faradic efficiency (FE%) of formic acid production, obtained during the electrolysis of CO2-SS at CuRE and CuRE/Sn.

Potential / V	-0.8		-1.3		-1.8	
	Concentration of formic acid / ppm	FE %	Concentration of formic acid / ppm	FE %	Concentration of formic acid / ppm	FE %
CuRE	9	1.2	215	5	985	8.3
CuRE/Sn	40	14.3	70	3.45	525	3.9

We can observe that the highest amount of formic acid is obtained at CuRE sample at -1.8 V, but the best performing electrode, in terms of faradic efficiency for formic acid production, seems to be the CuRE/Sn at -0.8 V. In any case, the very low FE values can be attributed to the vigorous H_2 evolution, which was always present as a side reaction at these potentials. However, it can be also observed that an undivided cell was adopted in the experiments. In this condition the re-oxidation of the product could occur, thus contributing to lowering the faradic yield. Other authors in the literature have reported similar problems and they tried to solve them by shielding the electrode surface by means a Nafion membrane (Du et al.,2017).

4. Conclusions

The proposed synthesis allows to obtain samples at which higher reductive currents are measured, compared to those obtained at commercial Cu or Sn foils, in $KHCO_3$ both in N_2 and CO_2 saturated solutions.
The different surface morphology could be responsible for a greater specific area, available for the reaction, but also different activity may be obtained for CO_2 reduction.
At all the synthesized samples, the reduction of CO_2 seems to occur to a certain extent, also at not very negative potential, but the total current measured in the presence of CO_2 is always lower than that measured in N_2 bubbled solutions. This result can be attributed to competition between active sites for H^+ and CO_2 reduction: the increase in current related to the CO_2 reduction does not compensate the decreasing current for H_2 evolution, and this results in a decrease of the total current.
Preliminary results from potentiostatic reductive tests indicate that formic and oxalic acid are the main products in the liquid phase, while H_2 evolution was always experimentally observed, and was responsible for the low faradic yield in formic acid. As the effect of Sn is considered, data indicated that formic acid production depends on the potential at which the reduction occurs: at higher negative potentials (-1.3 and -1.8V), CuRE/Sn showed FE lower than that measured at CuRE. Interestingly, a positive effect was observed at CuRE/Sn sample at the lowest investigated potential (-0.8V), at which even the low amount of Sn present in the sample was able to catalyse the formic acid formation, with a FE of 14%.
Investigations are ongoing to verify these preliminary results, and, in particular, to examine the effect of the Sn loading on the reaction path, and on the distribution of possible products.

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References

Centi G., Quadrelli E.A., Perathoner S., 2013, Catalysis for CO_2 conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries, Energy and Environmental Science, 6, 1711-1731.

Chen L., Guo Z., Wei X.G., Gallenkamp C., Bonin J., Mallart E.A., Lau K.C., Lau T.C., Robert M., 2015, Molecular Catalysis of the Electrochemical and Photochemical Reduction of CO_2 with Earth-Abundant Metal Complexes: Selective Production of CO vs HCOOH by Switching of the Metal Center, Journal of the American Chemical Society, 137, 10918-10921.

Du D., Lan R., Humphreys J., Tao S., 2017, Progress in inorganic cathode catalysts for electrochemical conversion of carbon dioxide into formate or formic acid, Journal of Applied Electrochemistry, 47, 661-678.

Gao S., Lin Y., Jiao X., Sun Y., Luo Q., Zhang W., Li D., Yang J., Xie Y., 2016, Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel, Nature, 529, 68-71.

Hara K., Kudo A., Sakata T., 1995, Electrochemical reduction of carbon dioxide under high pressure on various electrodes in an aqueous electrolyte, Journal of Electroanalytical Chemistry, 931, 141-147.

Hori Y., Murata A., Yoshinami Y., 1991, Adsorption of CO, intermediately formed in Electrochemical Reduction of CO_2, at a Copper Electrode, Journal of the Chemical Society, Faraday Transactions, 87, 125-128.

Hori Y., Takahashi I., Koga O., Hoshi N., 2002, Selective formation of C2 compounds from electrochemical reduction of CO_2 at a series of copper single crystal electrodes, The Journal of Physical Chemistry B, 106,15-17.

Hori Y., Wakebe H., Tsukamoto T., Koga O., 1994, Electrocatalytic process of CO selectivity in Electrochemical Reduction of CO_2 at metal electrodes in aqueous media, Electrochimica Acta, 39, 1833-1839.

Hossain M., De Lasa H.I., 2008, Chemical-looping combustion (CLC) for inherent CO_2 separations-a review, Chemical Engineering Science, 63, 4433-4451.

Kortlever R., Shen J., Schouten K.L.P., Calle-Vallejo F., Koper M.T.M., 2015, Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide, The Journal of Physical Chemistry Letters, 6, 4073-4082.

Lan Y., Ma S., Kenis P.J.A., Lu J., 2014, Hydrogen Evolution in the Presence of CO_2 in an Aqueous Solution during Electrochemical Reduction, International Journal of Electrochemical Science 9, 8097-8105.

Lim R.J., Xie M.S., Sk M.A., Lee J.M., Fisher A., Wang X., Lim K.H., 2014, A review on the electrochemical reduction of CO_2 in fuel cells, metal electrodes and molecular catalysts, Catalysis Today, 233, 169-180.

Merino-Garcia I., Albo J., Irabien A., 2017, Productivity and Selectivity of Gas-Phase CO_2 Electroreduction to Methane at Copper Nanoparticle-Based Electrodes, Energy Technology, 5, 1-8.

Raciti D., Livi K.J., Wang C., 2015, Highly dense Cu nanowires for low-overpotential CO_2 reduction, Nano Letters, 15, 6829-6835.

Sarfraz S., Garcia-Esparza A.T., Jedidi A., Cavallo L., Takanabe K., 2016, Cu-Sn bimetallic catalyst for selective aqueous electroreduction of CO_2 to CO, ACS Catalysis, 6, 2842-2851.

Schouten K.J.P., Gallent E.P., Koper M.T.M., 2014, The influence of pH on the reduction of CO and CO_2 to hydrocarbons on copper electrodes, Journal of Electroanalytical Chemistry, 716, 53-57.

Wang W.H., Himeda Y., Muckerma Y.T., Manbeck G.F., Fujita E., 2015, CO_2 Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO_2 Reduction, Chemical Reviews, 115, 12936-12973.

Wang Y., Zhou J., Lv W., Fang H., Wang W., 2016, Electrochemical reduction of CO_2 to formate catalysed by electroplated tin coating on copper foam, Applied Surface Science, 362, 394-398.

Yu X., Pickup P.G., 2008, Recent advances in direct formic acid fuel cells (DFAFC), Journal of Power Sources, 182, 124-132.