UDC 621.35

*Orest Kuntyi [a], Galyna Zozulya [a], Mariana Shepida [a], Roman Mnykh [a], Artur Mazur [a], Sergiy Korniy [b], Volodymyr Babizhetskyy [c], Anatoliy Zelinskiy [c]*

# CO$_2$ ELECTROREDUCTION IN AQUEOUS AND ACETONITRILE SOLUTIONS ON POROUS CATHODE FABRICATED BY ANODE DEZINCIFICATION OF CuZn

**Lviv Polytechnic National University, Lviv, Ukraine**
[b] **Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Lviv, Ukraine**
[c] **Ivan Franko National University of Lviv, Lviv, Ukraine**

The rates of the CO$_2$ electrochemical reduction were determined on porous cathodes formed by electrochemical dealloying of CuZn under different regimes of selective anodic dezincification of brass. It was established that the formation of a porous surface proceeds in two following stages: 1) the dissolution of Zn from the CuZn mainly along the grain boundaries with the formation of submicron crevices between them, and 2) electrochemical dezincification of brass grains and formation of nanopores. The zinc content in the nanoporous copper surface is less than 1%. It was proved that anodically dezincified brass porous cathodes demonstrate a significantly higher CO$_2$ reduction current on their surface than smooth copper and brass surfaces. For instance, in aqueous solutions, at an electrode potential of $-1.5$ V, the value of cathode current density on porous Cu cathodes is between 5 to 9 mA·cm$^{-2}$, while it is only 2.5 and 1.5 mA·cm$^{-2}$ on smooth Cu and CuZn cathodes, respectively. A similar trend is observed in an acetonitrile environment, where the current density of the CO$_2$ electroreduction at the electrode potential of $-3.0$ V is 22 to 27 mA·cm$^{-2}$, $\approx$15 mA·cm$^{-2}$, and $\approx$18 mA·cm$^{-2}$ on porous cathodes, Cu cathode, and CuZn cathode, respectively. As the pore size decreases from submicron to submicron-nanosized, there is a tendency for an increase in cathodic currents by approximately 80% and 25% in aqueous and in acetonitrile solutions, respectively. Additionally, CO$_2$ recovery on porous cathodes remains stable during long-term electrolysis at an electrode potential below $-1.5$ V.

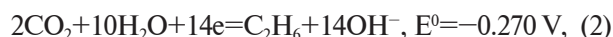**Keywords:** CO$_2$ electroreduction, KHCO$_3$ solution, Bu$_4$NClO$_4$ solution in acetonitrile, porous cathode, CuZn dezincification.

## Introduction

CO$_2$ emissions increase over the past three decades is one of the main environmental problems today [1]. Therefore, the issue of capturing and processing this gas belongs to priority scientific and engineering directions [2]. Recently, the main attention has been paid to the processing of CO$_2$ into the following valuable products: synthesis gas, methanol, methane, ethane, formic acid [2,3], etc. In the aspect of «green» technology, electrochemical conversion of carbon (IV) oxide [4] is especially promising.

Electrochemical reduction of CO$_2$ in aqueous solutions is a complex multistage process, during which the formation of transformation products occurs in a relatively narrow range of cathodic potentials (Eqs. (1)−(5)). Simultaneously, hydrogen is electrochemically evolved (Eq. (6)), its proportion being increased as the cathode potential increases.

$$CO_2 + 6H_2O + 8e = CH_4 + 8OH^-, \; E^0 = -0.240 \text{ V}, \quad (1)$$

$$2CO_2 + 10H_2O + 14e = C_2H_6 + 14OH^-, \; E^0 = -0.270 \text{ V}, \quad (2)$$

$$CO_2 + 5H_2O + 6e = CH_3OH + 6OH^-, \; E^0 = -0.380 \text{ V}, \quad (3)$$

$$CO_2 + H_2O + 2e = CO + 2OH^-, \; E^0 = -0.520 \text{ V}, \quad (4)$$

$$CO_2+2H_2O+2e=HCOOH+2OH^-, \ E^0=-0.610 \ V, \quad (5)$$

$$2H_2O+2e=H_2+2OH^-, \ E^0=-0.8277 \ V. \quad (6)$$

Over the last decade, there has been a growing interest in studying the electrochemical reduction of $CO_2$ in ionic liquids and organic aprotic solvents [5]. These non-aqueous environments are beneficial because they reduce the hydrogen evolution or prevent this undesirable process. Additionally, the number of products resulting from the electrochemical conversion of $CO_2$ decreases. For instance, reactions (7)−(9) occur in aprotic solvents, leading to the formation of oxalate and carbon (II) oxide [6]. The high electrochemical stability of organic aprotic solvents also allows for $CO_2$ conversion at electrode potential E=−3.0 ... −3.5 V without any side processes. This, along with the excellent solubility of carbon (IV) oxide, ensures a higher rate of $CO_2$ conversion than in aqueous solutions [5].

$$CO_2+e \rightarrow CO_2^-, \quad (7)$$

$$CO_2^-+CO_2^- \rightarrow (COO)_2^{2-}, \quad (8)$$

$$2CO_2+2e \rightarrow CO+CO_3^{2-}. \quad (9)$$

To ensure a high rate of $CO_2$ conversion, regardless of the nature of the environment, catalytically active cathodes are used, among which copper and copper-containing cathodes are the most studied [3−5]. Since the available surface area is the key to catalyst performance, high cathode surface area is required, and porous surface electrodes have recently received much attention [4,5,7].

One of the effective methods of preparing porous metals is electrochemical or chemical dealloying. They are based on the selective dissolution of the more electronegative metal of alloy. Chemical dealloying implies spontaneous electrochemical corrosion in the pickling solution takes place, while electrochemically induced dealloying involves anodic dissolution. The electrochemical dealloying is much more effective due to a higher dissolution rate and controlled formation of nanoporous and hierarchical porous structure. Relatively cheap commercial alloys, in particular brasses CuZn [8−14], are promising for dealloying in the commercial aspect. Their anodic dezincification occurs in electrolytes of different compositions with the formation of a porous surface (Table 1).

The purpose of the work is to determine the rates of the $CO_2$ electrochemical reduction in aqueous and acetonitrile solutions on porous cathodes formed by the electrochemical dealloying of brass (CuZn).

*Experimental*
*Materials and methods*
Electrochemical dezincification of brass (Cu62Zn38) was carried out in 0.2 M HCl solution at room temperature in potentiostatic mode for 10-, 15-, 20-, and 30-min. Voltammetric studies were carried out in a standard three-electrode electrochemical 50 mL cell. The working electrode was a brass plate (0.785 cm²), the counter electrode was platinum, and a silver chloride electrode was used as the reference electrode. The working electrode was polarized within potentials E=0; −0.1; and −0.2 V with respect to the silver chloride reference electrode. Before each experiment, the surface of the brass electrode was cleaned with sandpaper, washed with acetone, etched in a mixture of acids (nitric acid:sulfuric acid=1:2) for 5 s and then thoroughly washed with running and distilled water. All experiments were repeated three times. All solutions were prepared in distilled water using Sigma-Aldrich reagents. After dezincification, the samples were washed sequentially with water and isopropanol alcohol in an ultrasonic bath (Jeken Codyson CD-4800, 70 W output, and 42 kHz) for 30 s and dried at a temperature of 60⁰C.

*Cathode reduction of $CO_2$ on porous surface in acetonitrile solution*
The electrochemical reduction of carbon (IV) oxide was studied by cyclic voltammetry in the following solutions 1) 0.1 M aqueous solution of $KHCO_3$ and 2) 0.05 M tetrabutylammonium perchlorate ($Bu_4NClO_4$) solution of acetonitrile ($CH_3CN$), both solutions being saturated with $CO_2$ for 30 min. Voltammetric studies were performed in a standard 450 ml three-electrode electrochemical cuvette, utilizing round copper, brass, and porous dezincified of CuZn plates with an area of 0.785 cm², coated on the back side with varnish. We employed platinum as an auxiliary electrode and silver chloride electrode as a reference electrode. We registered cyclic voltammograms for the working electrodes in aqueous solutions with a potential sweep rate of 50 mV·s⁻¹ at E=0.0...−2.0 V. In acetonitrile, we conducted experiments at E=0.0...−3.0 V. Potentiostatic electrolysis in aqueous solutions was performed at E=−1.5; −1.8 V, while in acetonitrile at E=−3.0 V. We obtained cyclic polarization curves using an MTech PGP-550S potentiostat with a computer and a digital converter.

*Methods of analyses*
The morphology of the resulting porous surface was studied using a ZEISS EVO 40XVP scanning electron microscope. The image of the surface was obtained by recording secondary electrons by scanning an electron beam with energy of 20 keV. The chemical

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Table 1

**Conditions of the formation of porous surfaces by electrochemical dealloying of CuZn**

| Alloy | Electrolyte of dezincification | Electrode potential (current density) | Duration and temperature | Morphology of porous surface | Ref. |
|---|---|---|---|---|---|
| CuZn | 0.5 M NaCl+5 mM NaHCO$_3$ | 0.1 V (1.0 mA·cm$^{-2}$) | 24 h, 60$^0$C | porous structures with a pore depth of about 100 μm | [8] |
| CuZn | ChCl–urea DES | –0.4 V | 120$^0$C | 3D structures with a thickness of 150–450 nm | [9] |
| CuZn42 and CuZn21Si3P | MgSO$_4$+NaHCO$_3$+CaCl$_2$+Na$_2$SO$_4$ | –0.5...0.5 V (0...80 μA·cm$^{-2}$) | 0...1200 s, 75$^0$C | cubic crystals of Cu$_2$O (≈100 nm) evenly formed on the surface | [10] |
| Cu63/Zn37 | 0.1 M HCl | 0.2; 0.8; 1.3 V | 600, 900 s 20$^0$C | spherical and cubic particles >200 nm | [11] |
| CuZn30 and CuZn39 | 3% NaCl | –0.4; –0.15; 0.15 V | 15 min, 20$^0$C | cavities or holes on the surface and polygonal and cubic particles | [12] |
| CuZn38 | 0.05 M H$_2$SO$_4$ | 0.05 V; 0.1 V (1.6; 3.2 mA·cm$^{-2}$) | 50...2000 s, 20$^0$C | porous copper with a width of pores equal to 100...300 nm | [13] |
| CuZn38 | 0.01; 0.05; 0.1; 0.2; 0.4 M NaHSO$_3$ with/without 0.1 M NaCl | –0.2 V (0.2...1.8 mA·cm$^{-2}$) | 25$^0$C | hollow parts appearing on the surface | [14] |

composition of the surface was studied according to the results of energy dispersive integral maps analysis (EDX).

Phase analysis of the samples was performed using X-ray diffraction data. The XRD intensity data were collected on automatic diffractometer HZG-4a (CuK$_\alpha$-radiation, λ=1.54179 Å, 2θ$_{max}$=120$^0$, step-scan mode with a step size of 0.05$^0$ (2θ) and a counting time of 25−30 s per data point, Si calibration external standard). In this study, the program package FullProf Suite [15] was used for quantiыcation and calculation of structural parameters. SEM examination of the samples was carried out by using electron microscope Tescan Vega 3 LMU equipped with an X-MaxN 20 silicon drift detector. Overall compositions were investigated using energy-dispersive X-ray spectroscopy (EDX); gun voltage of 25 kV, shooting mode SE- and BSE-detectors, working distance of 15−16 mm, and vacuum of 10$^{-3}$ Pa.

*Results and discussion*

*Formation of porous surface of CuZn by electrochemical dezincification*

A significant difference in the standard electrode potentials values of the CuZn alloy components ($E^0_{Cu^{2+}/Cu}$=+0.34 V; $E^0_{Zn^{2+}/Zn}$=−0.76 V) is a favorable condition for the selective anodic dissolution of zinc with porous surface formation. However, dealloying of brass is a complex and multifactorial process, making it difficult to manage. Selective dissolution of zinc in brass occurred at the initial stage with the formation of a copper-enriched layer on the electrode surface. The value of anodic current is significant and it increases with increasing anodic potential during the active process of dezincification according to reaction (10) (Fig. 1). However, as the copper-enriched porous surface forms, reaction (10) slows down. This leads to the simultaneous course of reactions (10) and (11), that is, the leveling of the selective anodic dissolution of brass. However, the diffusion limitations in the pores slow down the process of removal of the formed Cu$^{2+}$-ions. This, as shown in articles [12,14], causes galvanic replacement according to reaction (12), which contributes to the enrichment of the pore surface with copper. Values of anodic currents increase with increasing of E$_{anode}$ (Fig. 1). However, at E=0.2 V, copper deposition is observed on the cathode surface, which indicates a significant share of the process of anodic dissolution of copper by reaction (11). Therefore, dezincification of brass was carried out at E=0.1 V.

$$Zn \rightarrow Zn^{2+}+2e, \qquad (10)$$

$$Cu \rightarrow Cu^{2+}+2e, \qquad (11)$$

$$Zn+Cu^{2+} \rightarrow Zn^{2+}+Cu. \qquad (12)$$
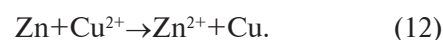
According to the SEM results (Fig. 2), the following structural changes occur on the brass surface during the electrochemical dezincification process. In the initial period, dissolution of Zn from the CuZn surface occurs mainly along the grain boundaries with the formation of crevices between them (Fig. 2,a).

Moreover, according to the EDX study results, the content of copper is 94 at.%. Over time, such crevices deepen with the formation of a microporous surface (Fig. 2,b). Prolonged electrolysis leads to electrochemical dezincification of brass grains. As a result, a nanoporous copper surface is also formed (Fig. 2,c), where the zinc content is less than 1 at.%.
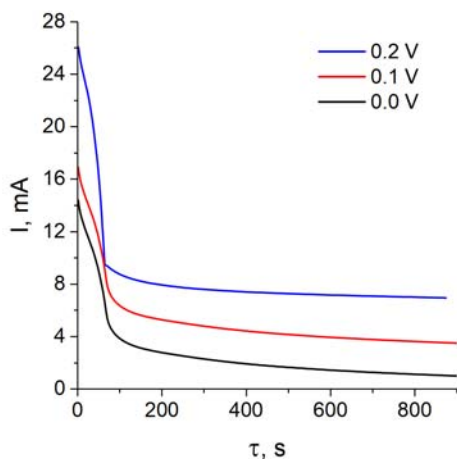


Fig. 1. Anode dezincification of CuZn in 0.2 M HCl solution at E=0.0; 0.1 and 0.2 V, t=20⁰C

In order to determine the lattice parameters and possible crystal structure transformations on the surface, the whole pattern fitting of Rietveld refinement was applied to the acquired XRD data. Figure 3 shows XRD patterns of different dezincificated CuZn surfaces. All peaks of the XRD patterns corresponds to two phases. The first phase is a cubic copper phase and the second is the solid solution zinc in copper. The results of refinements of four samples show nearly no changes of lattice parameters: a=3.619 Å for copper phase and a=3.705 Å for the second phase. They correspond to the literature data of copper and the $\alpha$-phase with highest zinc content. No shift of the peaks was observed. The peaks intensity of copper structure is fewest changed in comparison to the theoretical XRD pattern. For the second phase, the peak intensity assigned to [0 2 2] plane of Co/Zn $\alpha$-phase increases significantly, indicating the textured effects of the $\alpha$-phase surface. The refined coefficients of the preferred orientation using March-Dollase function changes slightly from 0.404(2) for Cu1 to 0.384(2) for Cu4. This value indicates predominant preferred platy orientation for the $\alpha$-phase. The refined fractional phase ratio (in %) for Cu to $\alpha$-phase increases as follows: Cu1 − 27(2):73(2), Cu2 − 33(1):67(1), Cu3 − 37(2):63(2), and Cu4 − 51(2):49(2). A small elevation of the background on all XRD patterns at 2θ=22−23⁰ indicates a little and constant part of the amorphized phase on the surface.

　　　　*CO₂ electroreduction in aqueous and acetonitrile*

*solutions on porous dezincificated CuZn cathodes*

In aqueous solutions, the current densities of $CO_2$ reduction on the CuZn cathode surface are smaller than on the copper cathode over the entire potential range of 0 V to −2 V (Fig. 4,a). This indicates the retarding effect of zinc on the process of electrochemical catalytic conversion of carbon (IV) oxide in $KHCO_3$ solutions. Badawy et al. [16] investigated the influence of zinc content in brass on the electrocatalytic reduction of $CO_2$ and explained this effect by the Zn ability to suppress the hydrogen evolution reaction. This is a logical explanation only for the potential region where hydrogen can be electrochemically generated (E<−0.82 V), since the overvoltage of $H_2$ evolution on the zinc cathode is sufficiently higher than on the copper. However, at E>−0.82 V, the $CO_2$ reduction current on the copper cathode also exceeds the value on the brass cathode (Fig. 4,a), which is unrelated to the overvoltage of hydrogen evolution. Therefore, it can be assumed that in an aqueous solution, this is due to Cu higher electrocatalytic activity than Zn.

$CO_2$ reduction currents in an aqueous solution on the porous cathode surface of anodically dezincified brass are three times higher than on smooth brass and twice higher than on copper (Fig. 4,b). A significant growth of the cathode current can be explained, first of all, by the porous and dezincified cathode surface. The last value of this quantity is commensurate with the value on Cu mesopore electrodes, which were prepared by using a thermal deposition process of copper on anodized aluminum oxide [17]. Moreover, as the pore sizes decrease from submicron (Fig. 4,b, curve Cu1) to submicron-nanosized (Fig. 4,b, curve Cu4), the cathode currents increase by ≈ 30%. The authors of the cited article explained this effect by the fact that nanoporous can change the local pH and retention time of key intermediates by confining the chemicals inside the pores. Therefore, a kind of capillary action is implemented, ensuring a stable concentration of the solution's components. In addition, the nanoporous copper catalyst is characterized by a decrease in the share of electrochemical hydrogen evolution at E<−1.5 V, which contributes to an increase in the percentage of electrochemical conversion of $CO_2$ [18].

It is important to note that the cathodic $CO_2$ reduction currents for copper and brass cathodes in an acetonitrile solution are practically identical up to E=≈2.5 V. However, at E=3.0 V, the currents are higher for the CuZn cathode (Fig. 4,c, copper and brass curves). Similarly to aqueous solutions, there is a trend of increasing cathode currents with greater cathode porosity (Fig. 4,c, Cu1, Cu3 and Cu4 curves).

Based on the findings (Fig. 5), it was observed that copper, brass, and porous dezincificated CuZn

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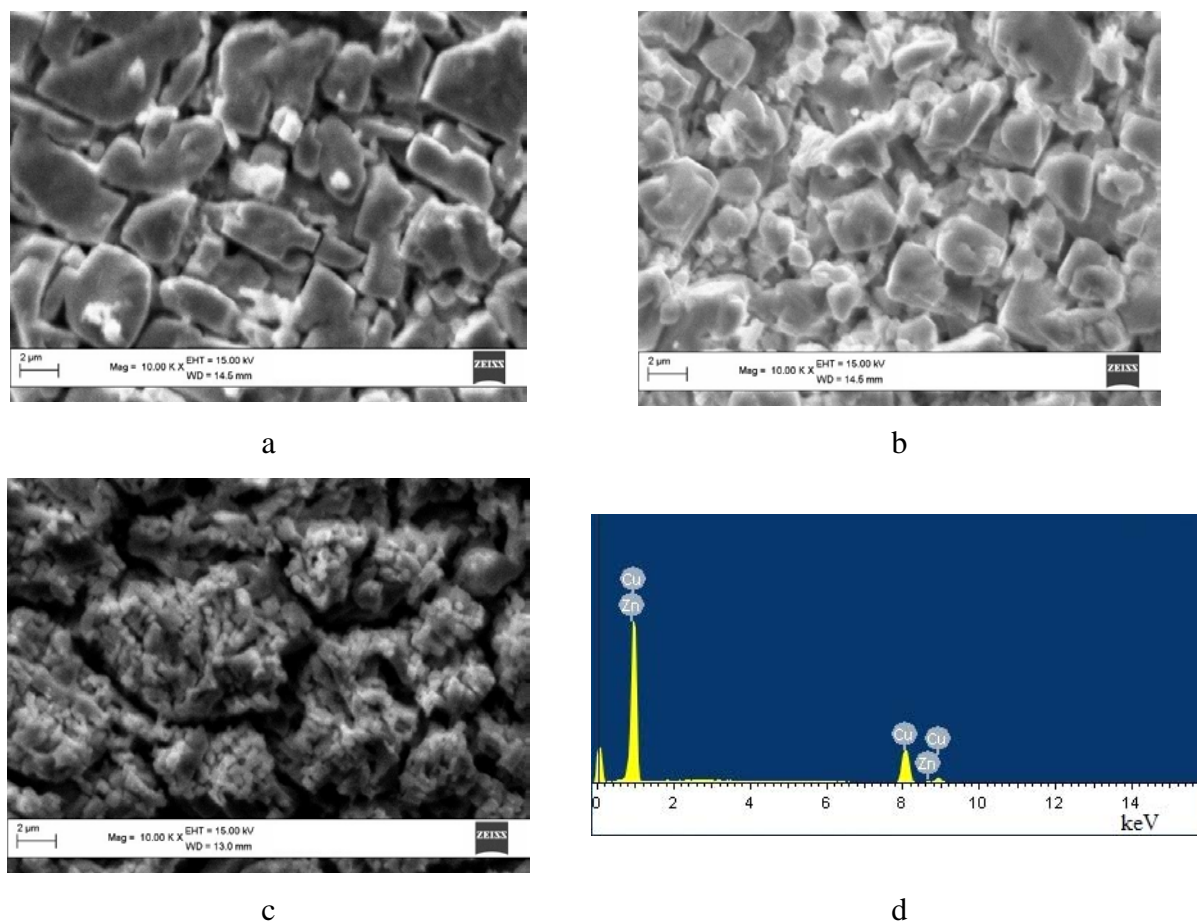
a



b



c



d

Fig. 2. SEM images of the porous surface electrode obtained by anodic dezincification of CuZn in 0.2 M HCl solutions for a duration of 10 (a), 20 (b) and 30 min (c) at E=0.1 V, t=20⁰C and EDX spectrum (d)
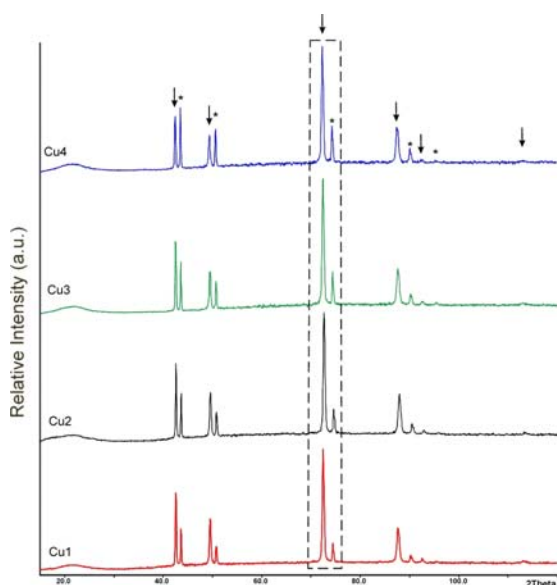


Fig. 3. XRD patterns of CuZn plate dezincificated in 0.2 M HCl solutions for a duration (min): 10 (Cu1), 15 (Cu2), 20 (Cu3) and 30 (Cu4). [0 0 2] peaks are highlighted by dashed line. Indicated reflections are from Cu (*) and α-phase (↓)

cathode exhibited a consistent cathode current value during extended electrolysis in both aqueous and acetonitrile solutions. This suggests that using a porous dezincificated CuZn cathode is a feasible option for the electrochemical reduction of $CO_2$.

### Conclusions

Electrochemical dealloying of brass CuZn in 0.2 M HCl at E=0.1 V occurs with selective dezincification. It results in the porous surface formation that undergoes the following stages: 1) the dissolution of Zn from the CuZn surface mainly along the grain boundaries with the formation of submicron crevices between them; and 2) formation of nanopores on the surface of the grain. The content of copper on the porous surface after the first stage of dealloying is 94 at.% at. and 99 at.% after the second one.

In an aqueous solution, $CO_2$ reduction current on the porous cathode surface of anodically dezincified brass is three times higher than on smooth brass and twice higher than on copper. As the pore sizes decrease from submicron to submicron-nanosized, the cathode current increase by ~30%. So, for E=−1.5 V, porous Cu cathodes have a value of $i_{cathode}$ in the range of
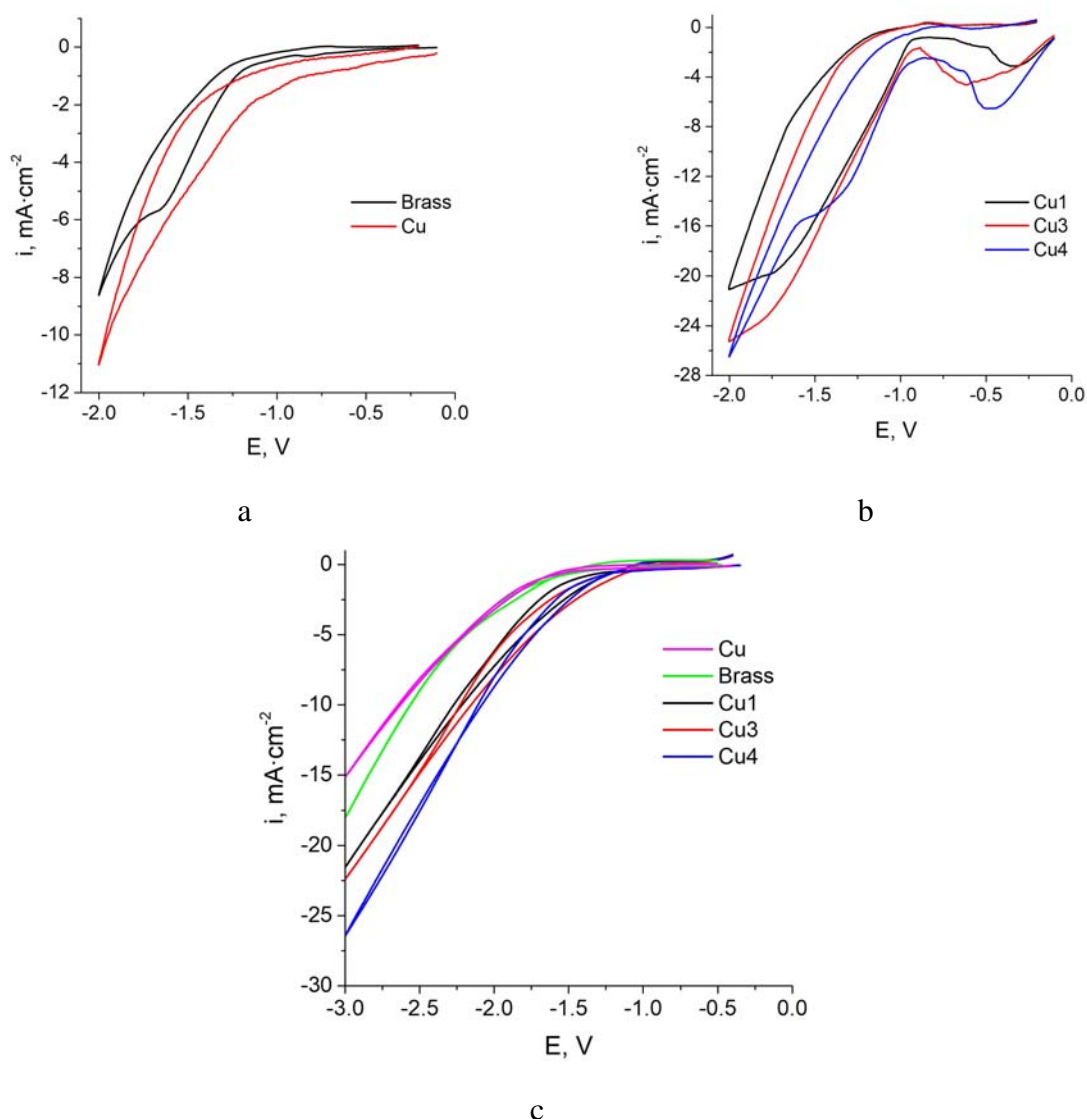
Fig. 4. Cyclic voltammograms of brass and Cu (a); and Cu1; Cu3; and Cu4 (b) electrodes in $CO_2$-saturated 0.1 M $KHCO_3$ aqueous (*a, b*) and 0.05 M $Bu_4NClO_4$ acetonitrile (*c*) solutions

5−9 mA·cm$^{-2}$. Smooth Cu and CuZn have lower cathode current densities: 2.5 and 1.5 mA·cm$^{-2}$, respectively. The electrochemical reduction of $CO_2$ on the obtained porous surface at E$<$−1.5 V, where high i$_{cathode}$ values are provided, is stable during long-term electrolysis. In the acetonitrile solution on the porous cathode surface of anodically dezincified brass, a similar trend of increasing the cathode current density of $CO_2$ reduction is observed with increasing the surface porosity. Specifically, porous cathodes at E=−3.0 V yield 22 to 27 mA·cm$^{-2}$, while Cu and CuZn yield ≈15 and ≈18 mA·cm$^{-2}$, respectively.

The $CO_2$ recovery is stable in aqueous and acetonitrile solutions during long-term electrolysis on a porous cathode.

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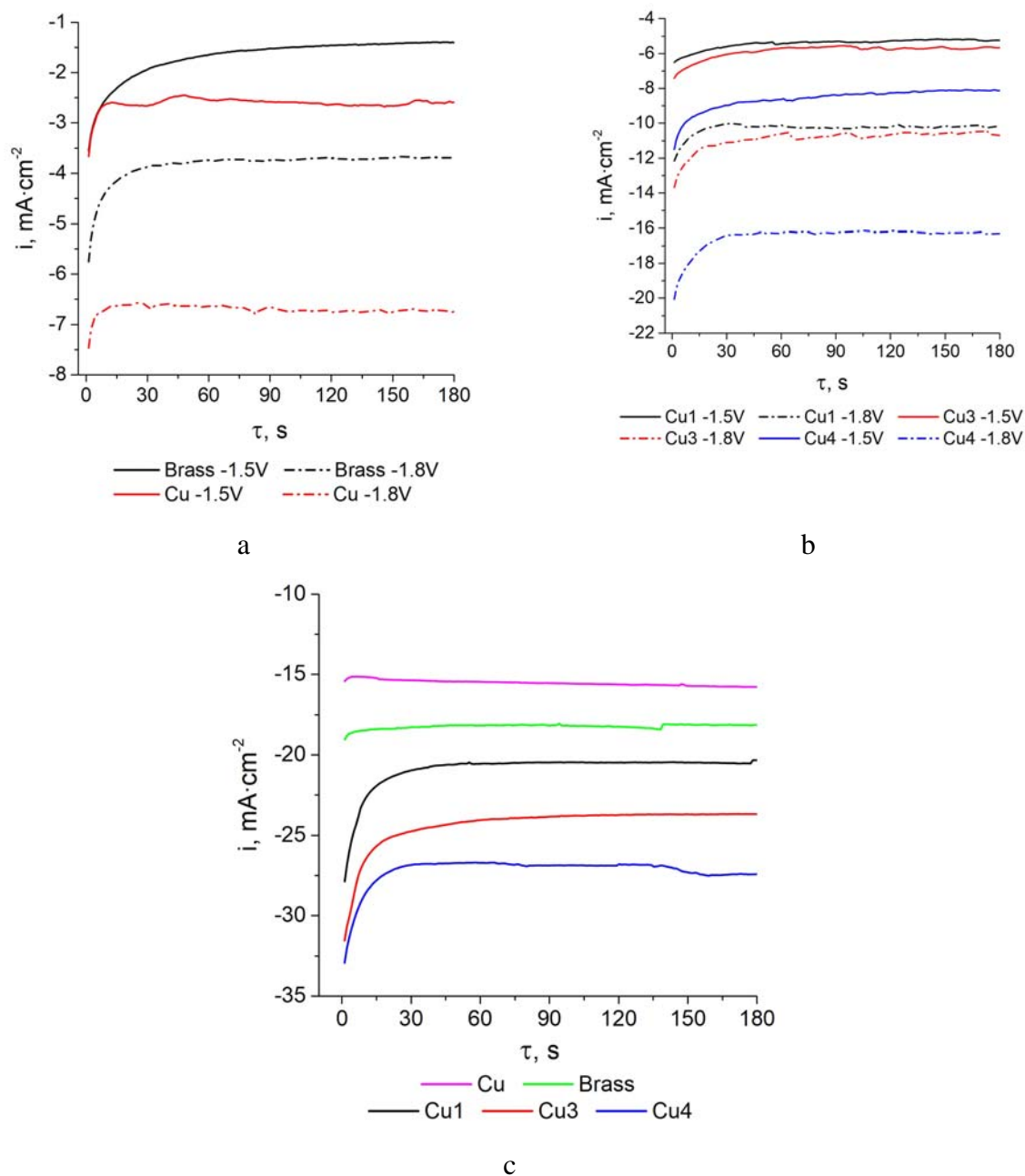
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Fig. 5. Current density vs. time curves recorded for potentiostatic electrolysis on copper, brass and dezincificated CuZn cathode in $CO_2$-saturated 0.1 M $KHCO_3$ aqueous (*a, b*) and 0.05 M $Bu_4NClO_4$ acetonitrile (*c*) solutions

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## ЕЛЕКТРОВІДНОВЛЕННЯ CO$_2$ У ВОДНИХ ТА АЦЕТОНІТРИЛЬНИХ РОЗЧИНАХ НА ПОРУВАТИХ КАТОДАХ, СФОРМОВАНИХ АНОДНИМ ЗНЕЦИНКУВАННЯМ CuZn

*О. Кунтий, Г. Зозуля, М. Шепіда, Р. Мних, А. Мазур, С. Корній, В. Бабіжецький, А. Зелінський*

Швидкість електрохімічного відновлення CO$_2$ була визначена на поруватих катодах, сформованих електрохімічним делегуванням CuZn за різних режимів селективного анодного знецинкування латуні. Встановлено, що формування поруватої поверхні відбувається стадійно: 1) розчинення Zn із CuZn переважно вздовж межі зерен з утворенням субмікронних щілин між ними; 2) електрохімічне знецинкування зерен латуні та утворення нанопор. Вміст цинку в нанопоруватій мідній поверхні становить менше 1%. Було доведено, що на поверхні поруватого катода, сформованого анодним знецинкуванням латуні, струми відновлення CO$_2$ значно вищі, ніж на гладких поверхнях міді і латуні. Так, у водних розчинах за E=−1,5 В на поруватих Cu катодах i$_{cathode}$=5−9 мА/см$^2$, тоді як на гладких Cu і CuZn 2,5 і ≈1,5 мА/см$^2$, відповідно. Аналогічний ефект має місце у ацетонітрильному середовищі: 22−27 мА/см$^2$ на поруватих катодах, ≈15 і ≈18 мА/см$^2$ на Cu і CuZn за E=−3,0 В. Зі зменшенням розміру пор від субмікронних до субмікронно-нанорозмірних спостерігається тенденція до збільшення катодних струмів на ≈80% у водних розчинах і ≈25% в ацетонітрильних. При довготривалому електролізі на поруватому катоді за E<−1,5 В відновлення CO$_2$ є стабільним.

**Ключові слова**: електровідновлення CO$_2$, розчин KHCO$_3$, розчин Bu$_4$NClO$_4$ в ацетонітрилі, поруватий катод, знецинкування CuZn.

## CO$_2$ ELECTROREDUCTION IN AQUEOUS AND ACETONITRILE SOLUTIONS ON POROUS CATHODE FABRICATED BY ANODE DEZINCIFICATION OF CuZn

*Orest Kuntyi [a], Galyna Zozulya [a], Mariana Shepida [a, *], Roman Mnykh [a], Artur Mazur [a], Sergiy Korniy [b], Volodymyr Babizhetskyy [c], Anatoliy Zelinskiy [c]*

[a] **Lviv Polytechnic National University, Lviv, Ukraine**

[b] **Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Lviv, Ukraine**

[c] **Ivan Franko National University of Lviv, Lviv, Ukraine**

[*] **e-mail: maryana_shepida@ukr.net**

The rates of the CO$_2$ electrochemical reduction were determined on porous cathodes formed by electrochemical dealloying of CuZn under different regimes of selective anodic dezincification of brass. It was established that the formation of a porous surface proceeds in two following stages: 1) the dissolution of Zn from the CuZn mainly along the grain boundaries with the formation of submicron crevices between them, and 2) electrochemical dezincification of brass grains and formation of nanopores. The zinc content in the nanoporous copper surface is less than 1%. It was proved that anodically dezincified brass porous cathodes demonstrate a significantly higher CO$_2$ reduction current on their surface than smooth copper and brass surfaces. For instance, in aqueous solutions, at an electrode potential of −1.5 V, the value of cathode current density on porous Cu cathodes is between 5 to 9 mA·cm$^{-2}$, while it is only 2.5 and 1.5 mA·cm$^{-2}$ on smooth Cu and CuZn cathodes, respectively. A similar trend is observed in an acetonitrile environment, where

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the current density of the $CO_2$ electroreduction at the electrode potential of −3.0 V is 22 to 27 mAcm$^{-2}$, ≈15 mA·cm$^{-2}$, and ≈18 mA·cm$^{-2}$ on porous cathodes, Cu cathode, and CuZn cathode, respectively. As the pore size decreases from submicron to submicron-nanosized, there is a tendency for an increase in cathodic currents by approximately 80% and 25% in aqueous and in acetonitrile solutions, respectively. Additionally, $CO_2$ recovery on porous cathodes remains stable during long-term electrolysis at an electrode potential below −1.5 V.

**Keywords:** $CO_2$ electroreduction; KHCO$_3$ solution; Bu$_4$NClO$_4$ solution in acetonitrile; porous cathode; CuZn dezincification.

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