Electrochemical CO_2 Reduction

5% of total								
Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	**Total**
Points	2	8	3	3	5	8	4	**33**
Score								

In recent years, the electrochemical conversion of CO_2 into higher value products has been considered a promising and technologically feasible approach to mitigate the negative climatic effects caused by its increasing levels in the atmosphere. Several technologies have been developed to achieve this goal. Among these, CO_2 reduction through electrochemical means (CO_2RR) warrants particular attention due to its ability to be powered by renewable energy to transform environmentally harmful CO_2 into platform chemicals.

Electrocatalysts are essential not only to accelerate the intrinsically slow CO_2RR but also to direct the electrolysis reaction towards the desired reaction products (product selectivity). In this context, it is not only the chemical nature of the catalyst itself which governs the resulting CO_2RR product distribution but also its morphological characteristics on various length scales. A new concept of CO_2RR catalyst design relies on the electrodeposition of foam-type materials, which offer a large surface area that is accessible to reactants (e.g. H_2O, H_2, and CO_2). Copper-based materials are the only known metallic CO_2RR catalysts that can produce hydrocarbons and alcohols in significant amounts from CO_2 electrolysis.

Given below are thermodynamic data of selected substances:

	$\triangle_f H^\ominus$ kJ mol^{-1}	$S^\ominus$, J mol^{-1} K^{-1}
H_2O (l)	-285.83	69.95
O_2 (g)	0	205.15
H_2 (g)	0	130.68
CO_2 (g)	-393.52	213.79
ethanol (l)	-276.00	159.86
***n*-propanol (l)**	-302.54	192.80

Table 1. Standard formation enthalpy $\triangle_f H^\ominus$ and standard entropy $S^\ominus$ for some substances under standard conditions ($T = 298.15$ K, $p = 1$ bar).

Cell reaction	E, V vs. SHE
$Cu^{2+} + 2e^{-} \longleftrightarrow Cu$	+0.34
$2H^{+} + 2e^{-} \longleftrightarrow H_2$	0.00

Table 2. Selected half-cell reactions and corresponding standard potentials under the standard conditions.

2.1	**Write and balance** the chemical equation of the half-cell reactions for the following electrochemical reduction processes in acidic environment (i) CO_2 to ethanol; (ii) CO_2 to *n*-propanol.	2pt

2.2	**Combine** the half-cell of the reduction process with an $H_2/2H^+$ half-cell where the latter acts as anode. **Calculate** the value of the standard cell potential of the CO_2 to **ethanol** reduction.	8pt

Cu foam electrodeposition processes (see Figure 1) were carried out in an aqueous $1.5\ \mathrm{M}$ sulfuric acid solution containing $0.2\ \mathrm{M}$ copper sulfate ($CuSO_4{\cdot}5H_2O$) as the copper source. A Cu disk ($1\ \mathrm{cm}^2$) and a Pt foil served as the cathode and the anode, respectively.

2.3	**Write** all the reduction and oxidation half-cell reactions taking place at the cathode and the anode, respectively.	3pt

Figure 1 shows the principle of dynamic hydrogen bubble-templated metal deposition.

Figure 2 displays top-down scanning electron microscopy (SEM) images of three different Cu foams obtained upon interruption of the metal deposition at different times: $5\ \mathrm{s}$, $20\ \mathrm{s}$, and $80\ \mathrm{s}$

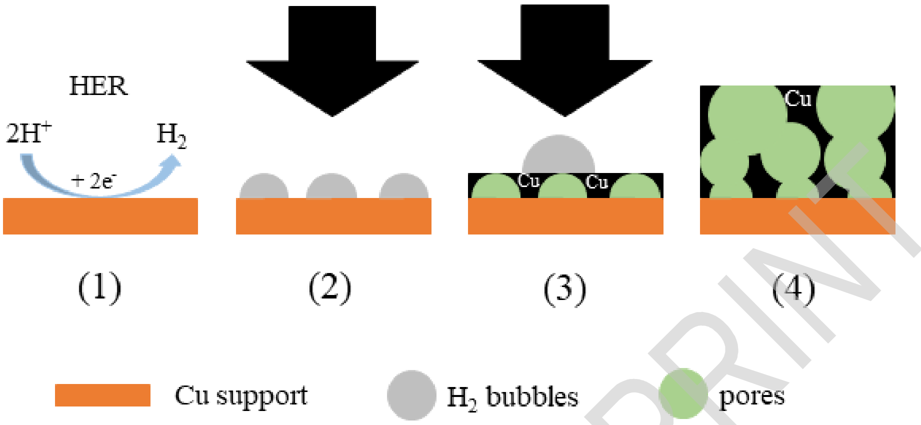

Figure 1. Depiction of the electrodeposition of foam-type materials. In the course of electrochemical metal deposition (black arrows) at high current densities in aqueous media, the Hydrogen Evolution Reaction (HER) takes place on the metallic (Cu) support (1). The surface becomes thus partially covered by H_2 bubbles (2). The H_2 bubbles act as a template for metal deposition (3). As a result a highly porous metal foam emerges (4).

2.4 Considering this mechanism, **assign** the correct deposition time to the Cu foams shown in **Figure 2 on the answer sheet (white boxes upper left corner)**. 3pt

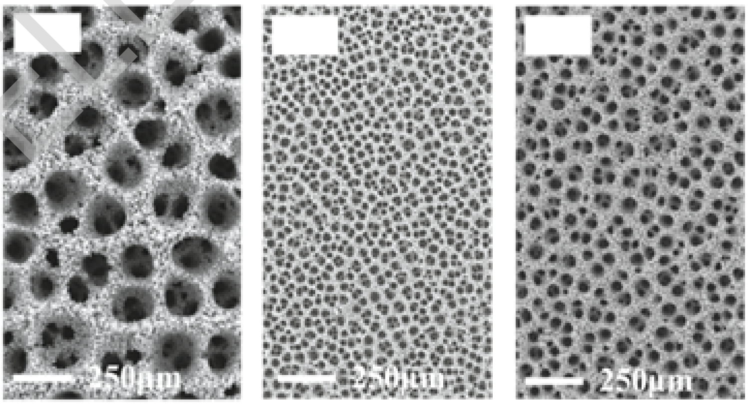

Figure 2. Cu foams obtained by galvanostatic Cu electrodeposition at a current density of $j = -3\ \mathrm{A\ cm^{-2}}$ The deposition was, in each case, interrupted at distinct elapsed duration: $5\ \mathrm{s}$, $20\ \mathrm{s}$, and $80\ \mathrm{s}$. The scale bar is the same in all panels.

Bimetallic CuAg systems are excellent catalysts for the electrosynthesis of alcohols from CO_2. $5.4\ \mathrm{mg}$ of a bimetallic Cu-Ag foam catalyst ($90\ \mathrm{wt.\%\ Cu},\ M_{Cu} = 63.546\ \mathrm{g}\ mol^{-1};\ 10\ \mathrm{wt.\%\ Ag},\ M_{Ag} = 107.868\ \mathrm{g}\ mol^{-1}$) was galvanostatically deposited onto a Cu foil ($1\ \mathrm{cm}^2$) at a current density of $j = -3\ \mathrm{A\ cm}^{-2}$ applied for $20\ \mathrm{s}$ (the minus sign accounts for a reductive/cathodic process).

2.5	**Calculate** the Faradaic efficiency (FE in %) of this metal deposition process. FE is defined as $Q_{\text{product}}/Q_{\text{total}} \cdot 100\%$. Q denotes the charge.	5pt

We consider a CO_2 electrolysis experiment carried out in $35\ \mathrm{mL}$ CO_2-saturated $0.5\ \mathrm{M}$ $KHCO_3$ electrolyte solution over the bimetallic Cu-Ag foam catalyst ($90\ \mathrm{wt.\%\ Cu};\ 10\ \mathrm{wt.\%\ Ag}$). The CO_2 electrolysis was carried out at a constant (total) current density of $j(tot) = -30\ \mathrm{mA\ cm}^{-2}$ for $3600\ \mathrm{s}$ (note the current density is normalized to the geometric surface area of $1\ \mathrm{cm}^2$; the minus sign accounts for a reductive/cathodic process). A product analysis, carried out after the electrolysis, revealed mass concentrations of $41.3\ \mathrm{mg\ L}^{-1}$ and $7.4\ \mathrm{mg\ L}^{-1}$ for ethanol and *n*-propanol, respectively. Both alcohols are liquid reaction products and accumulate in the electrolyte in the course of the electrolysis reaction. We assume that gaseous hydrogen (H_2) is formed as the only by-product of the process.

2.6	**Calculate** the current densities required for the formation of (a) ethanol ($MW_{\text{ethanol}} = 46.08\ \mathrm{g\ mol}^{-1}$) and (b) *n*-propanol ($MW_{n\text{-propanol}} = 60.10\ \mathrm{g\ mol}^{-1}$) assuming that the current densities do not change with electrolysis time.	8pt

2.7	**Calculate** the volume of the formed hydrogen on the 1 cm^2 catalyst area at 298.15 K and 1 bar, assuming ideal behavior of the formed hydrogen, and its complete release into the gas phase. *If you did not get a result in **Task 2.5**, continue with* $FE_{(EtOH)} = 45.1\%$ *and* $FE_{(PrOH)} = 4.8\%$.	4pt