Supplementary Materials:

Electrochemical formation of copper phosphide from aqueous solutions of Cu(II) and hypophosphite ions

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LM and RV current address: "2" and "3" respectively.

Part 1 contains the scripts written in Python 3.8, on a Jupyter Notebook, that were used for the transient analysis according to equation (4), calculating *zp* as defined on equation (8) to find the solution of the system of equations (9), as well as calculation of N_{si} (10) as seen in the research paper.

Data for analysis are contained in the files "280mV.csv" and "280mV-Cu.csv" corresponding to current transient registered at 280 mV vs. Cu/Cu^{2+} in the presence and absence of hypophosphite, respectively.

The file called "supplementary_material_algorithm.ipynb" contains the Python scripts that reads the data files and performs the calculations. Below are its content and results.

Part 2 presents further evidence as a comparison of current transients, SEM images, and additional analysis only on the presence of Cu(II).

Part 1: Analysis of current transients in terms of the theory for the nucleation and 3D growth of a new binary phase under diffusion control

Necessary packages to run the scripts

[2]:
```
import pandas as pd
import matplotlib.pyplot as plt
import numpy as np
from scipy import optimize,integrate
from scipy.optimize import curve_fit
```

0.1 parameters

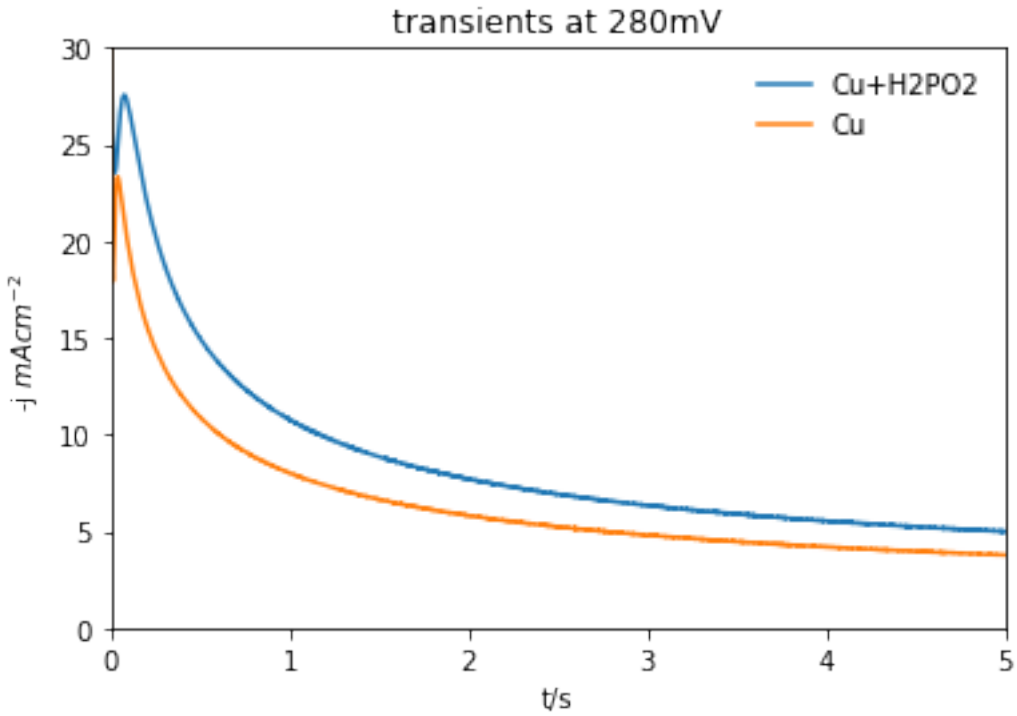
[3]:
```
#Cu
z1=2
Dcu=3.80586407347027E-06
x1=0.5
v1=7.0921875
#HP
z2=1
x2=0.5
Dhp=0.00001225
v2=20.31318681
F=96485
c=0.00004
gamma=1
Dw=(z1*Dcu*gamma +z2*Dhp)/(gamma*(z1*x1+z2*x2))
Da=(gamma*Dcu+Dhp)/(gamma+1)
k=np.sqrt(8*np.pi*c*(0.977*v1+0.023*v2)/(gamma*(z1*0.977+z2*0.023)*(1+gamma)))
a= Dw*F*c/(np.pi*Da)**0.5
area = 0.21
print(f'Dw={Dw},Da={Da},k={k}')
```

```
Dw=1.3241152097960361e-05,Da=8.027932036735135e-06,k=0.04336486368571909
```

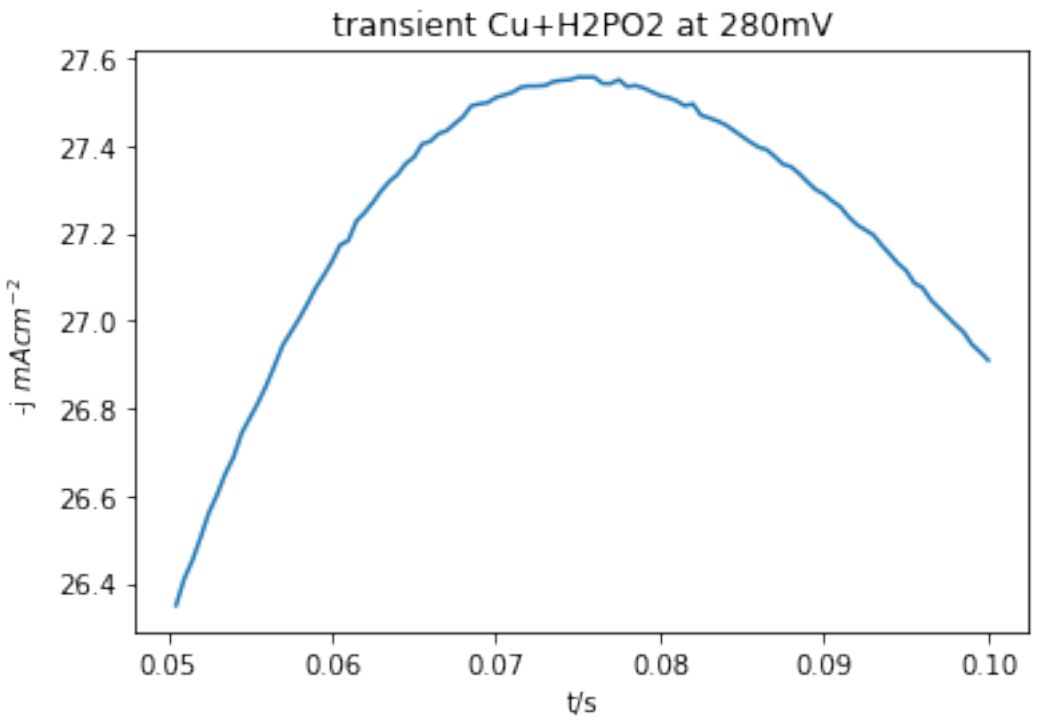
[4]:
```
#Cu2+ 0.04M + H2PO2- 0.04M, at 280mV
CuP280 = pd.read_csv("280mV.csv",header=0,sep='[,:]',engine='python')
xhp = CuP280["T"]
yhp = CuP280["i"].apply(lambda x: x*1000/(-area))

#Cu2+ 0.04M, at 280mV
Cu280 = pd.read_csv("280mV-Cu.csv",header=0,sep='[,:]',engine='python')
xCu = Cu280['T']
yCu = Cu280['i'].apply(lambda x: x*1000/(-area))
```

0.2 current transients analysis

[5]:
```
ax = plt.axes()
ax.plot(xhp,yhp,label='Cu+H2PO2')
ax.plot(xCu,yCu, label='Cu')
ax.set(ylim=(0, 30), xlim=(0,5),
       xlabel='t/s',ylabel='-j $mAcm^{-2}$',
       title='transients at 280mV');
ax.legend(loc='upper right', frameon=False, fontsize=10)
plt.show()
```



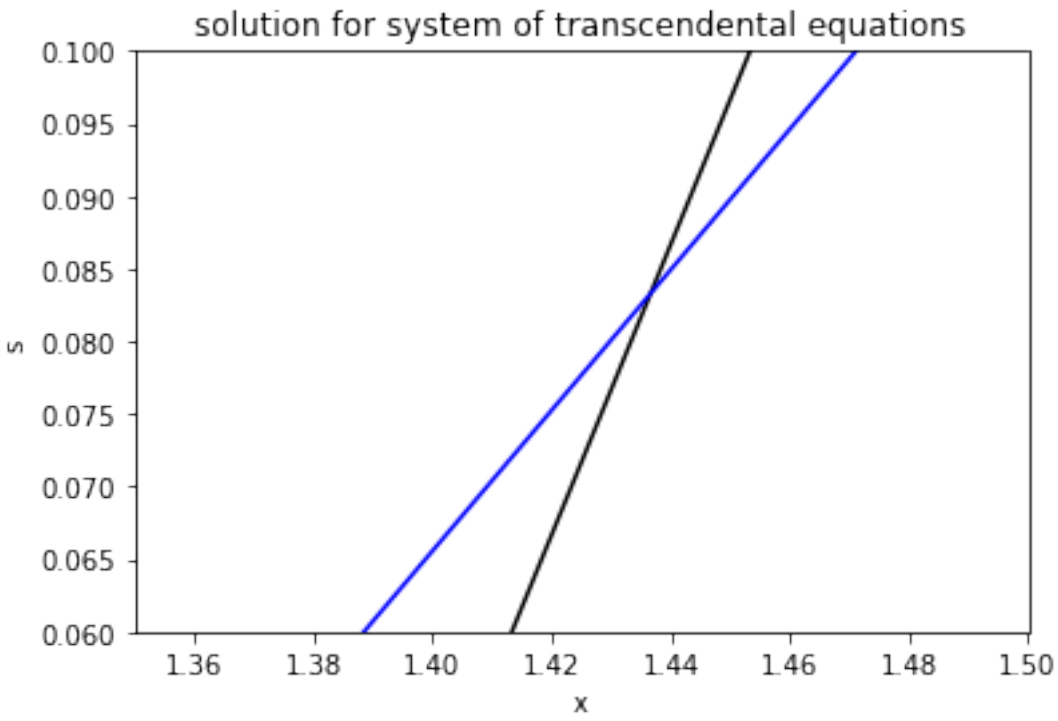
[6]:
```
ax = plt.axes()
ax.plot(xhp.iloc[100:200],yhp.iloc[100:200])
i_max=yhp.iloc[100:200].max()/1000
t_max =CuP280[yhp == i_max*1000]['T'].iloc[0]
ax.set(xlabel='t/s',ylabel='-j $mAcm^{-2}$',
       title='transient Cu+H2PO2 at 280mV');
plt.show()
print(f'i_max = {i_max} and t_max = {t_max} for Cu+H2PO2 at 280 mV')
```




```
i_max = 0.027556333333333335 and t_max = 0.075 for Cu+H2PO2 at 280 mV
```

0.2.1 system of transcendental equations

[7]:
```
def ec1(x,s):
    return np.log(1-((i_max*t_max**0.5)/a))+x-s*(1-np.exp(-x/s))

def ec2(x,s):
    return np.log(1+2*x*(1-np.exp(-x/s)))-x + s*(1-np.exp(-x/s))

x=np.linspace(0.000001, 15,num=100)
s=np.linspace(0.000001, 10,num=100)
X,Y = np.meshgrid(x, s)
Z1= ec1(X,Y)
Z2= ec2(X,Y)

ax = plt.axes()
ax.contour(X,Y,Z1,[0], colors='black')
ax.contour(X,Y,Z2,[0], colors='blue')
ax.set(xlabel='x',ylabel='s',xlim=(1.35,1.5),ylim=(0.06,0.10),
      title='solution for system of transcendental equations')
plt.show()
```

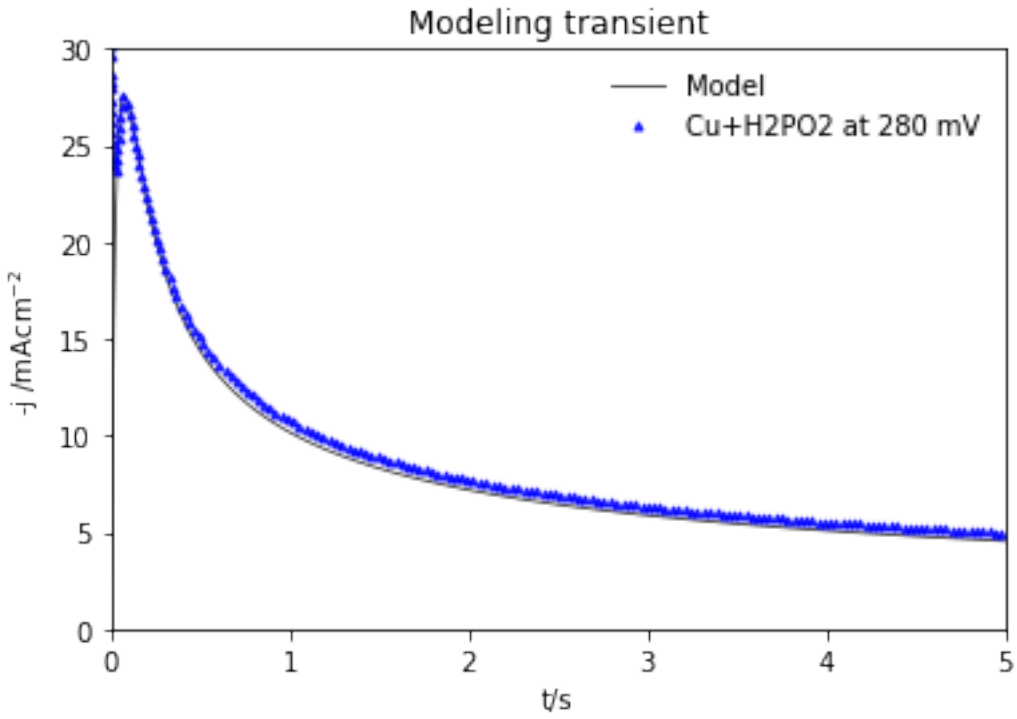


[8]:
```
def system(args):
    x=args[0]
    s=args[1]
    return [np.log(1-((i_max*t_max**0.5)/a))+x-s*(1-np.exp(-x/s)),
       np.log(1+2*x*(1-np.exp(-x/s)))-x + s*(1-np.exp(-x/s))]

initial_guess=[1.44,0.09]

#minimization using Levenberg-Marquardt algorithm
root=optimize.root(system,initial_guess, method='lm')

x,s=root.x
N0=x/(np.pi*k*(Da**0.5)*(Dw**0.5)*t_max)
A=(N0*np.pi*k*(Da**0.5)*(Dw**0.5))/s
print(f'x={x},s={s}, N0={N0}, A={A}')
```

```
x=1.4351578793636632,s=0.08182180411307736, N0=13623410.011465028,
A=233.86722645555972
```

[9]:
```
t = np.linspace(0.00005,5,1000)
model = Dw*F*c/(np.sqrt(np.pi*Da*t))*(1-np.exp(-N0*np.pi*k*np.
 ↪sqrt(Da*Dw)*(t-((1-np.exp(-A*t))/A))))
```

```
ax = plt.axes()
ax.plot(t, model*(1000), color="black",alpha=0.8,
        linewidth=0.8, linestyle="-",label="Model")
ax.plot(xhp, yhp, color='blue',alpha=0.8,
        linewidth=0.1,linestyle="None",marker='^',
        markersize=3,markevery =0.01,label='Cu+H2PO2 at 280 mV')

ax.set(xlabel='t/s',ylabel=r'-j /mAcm$^{-2}$', xlim=(0,5), ylim=(0,30),
       title='Modeling transient')
ax.legend(loc='upper right', frameon=False, fontsize=10)
plt.show()
```



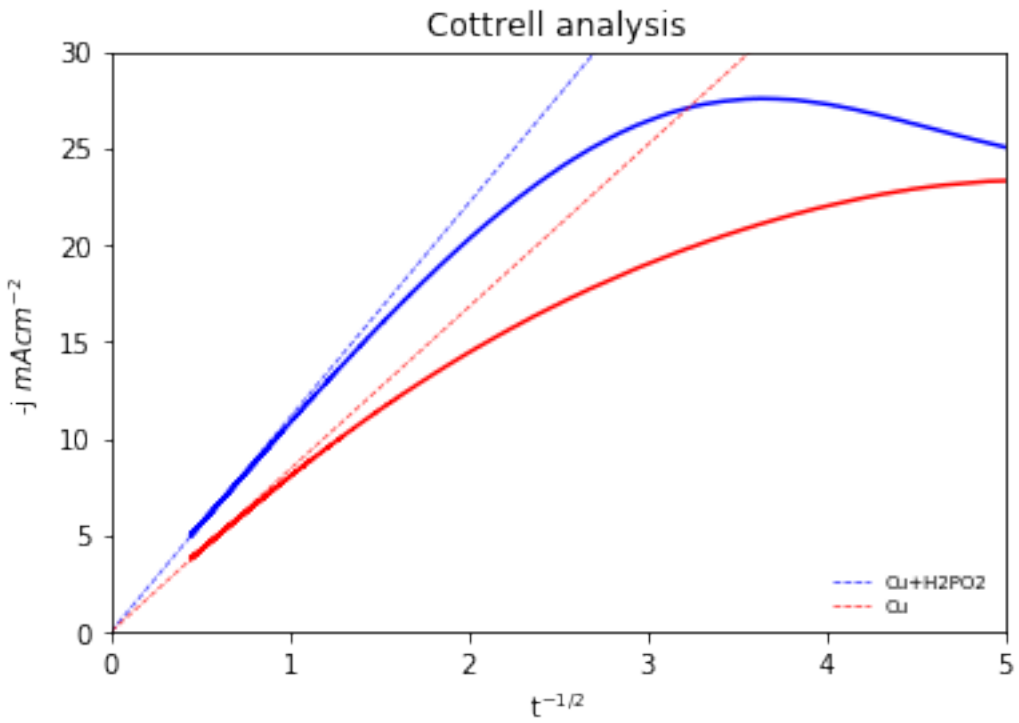
0.2.2 the saturation number density of nuclei: Ns

[10]:
```
def integral(u):
    return np.exp(-N0*np.pi*k*np.sqrt(Dw)*np.sqrt(Da)*
                  (A*u-1-np.exp(-A*u))/A)*np.exp(-A*u)

area= integrate.quad(integral,0,30)
Ns=A*N0*area[0]
print(f'integral={area[0]},Ns={Ns}')
```

```
integral=0.004477061212917151,Ns=14264226.453074059
```

0.2.3 Cottrell analysis

[11]:
```
#data
xp_Cottrell = xhp.apply(lambda x: x**(-0.5) )
x_Cottrell = xCu.apply(lambda x: x**(-0.5) )
ax = plt.axes()
#fit trend
def poly(x,a):
    return x*a

slope_p=curve_fit(poly, xp_Cottrell.iloc[7000:8500], yhp.iloc[7000:8500])[0]
slope_cu=curve_fit(poly, x_Cottrell.iloc[7000:8500], yCu.iloc[7000:8500])[0]
poly_x =np.linspace(0.00000, 5,num=100)

#data
ax.plot(xp_Cottrell, yhp,color='blue')
ax.plot(x_Cottrell, yCu, color='red')
#fit trend
ax.plot(poly_x,slope_p*poly_x,color="blue",alpha=0.8,linewidth=0.75,
        linestyle="--", label='Cu+H2PO2')
ax.plot(poly_x,slope_cu*poly_x,color="red",alpha=0.8,linewidth=0.75,
        linestyle="--",label='Cu')
ax.legend(loc='lower right', frameon=False, fontsize=7)
ax.set(xlabel='t$^{-1/2}$',ylabel='-j $mAcm^{-2}$',xlim=(0,5), ylim=(0,30),
       title='Cottrell analysis')
plt.show()
```

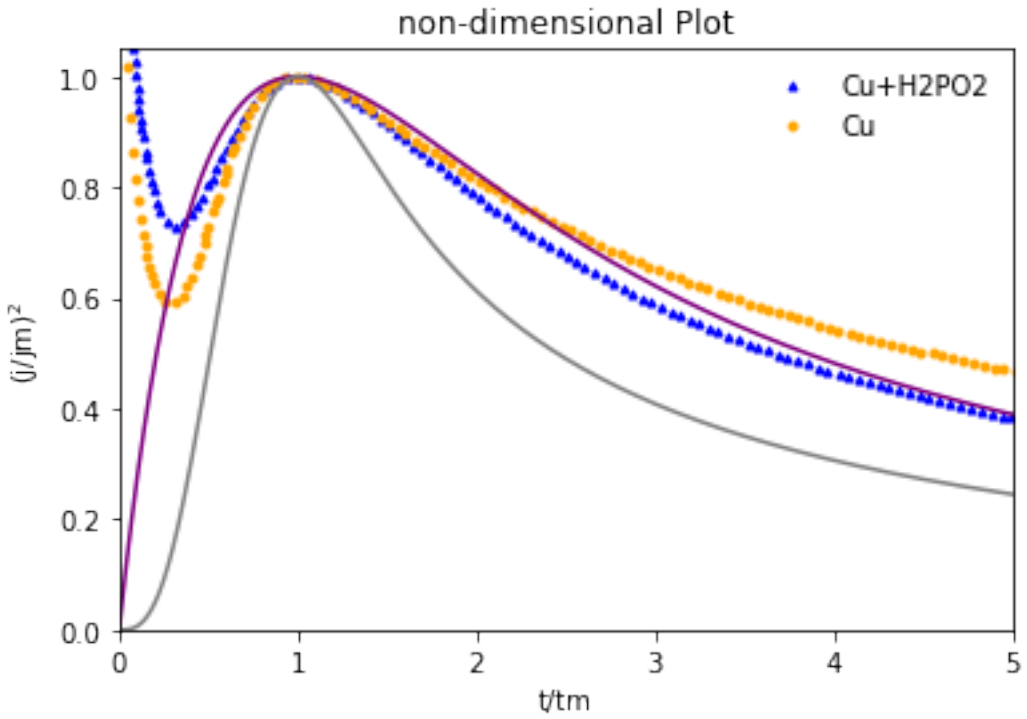


[12]:
```
jj=slope_p/slope_cu
zp=int((z1*gamma*(jj*z1*np.sqrt(Dcu*Da)*x1-Dcu))/
       (Dhp-jj*z1*np.sqrt(Dcu*Da)*gamma*x2))

Dapp=(Dw/Da**0.5)**2
Dexp= (slope_p*np.pi**0.5/(F*1000*c))**2
print(f'zp={zp},Dapp={Dapp},Dexp={Dexp}')
```

```
zp=1,Dapp=2.1839759987881508e-05,Dexp=[2.58162763e-05]
```

0.2.4 non-dimensional anlysis

[13]:
```
ta = np.linspace(0.00001,5,1000)
inst= (1.9542/ta)*(1-np.exp(-1.2564*ta))**2
prog=(1.2254/ta)*(1-np.exp(-2.3367*ta**2))**2

adidata = pd.DataFrame()
adidata['t/tm']=xhp.apply(lambda x:x/t_max)
adidata['i/im']=yhp.apply(lambda x:(x/(i_max*1000))**2)

i_maxCu=yCu.iloc[20:200].max()/1000
t_maxCu=Cu280[yCu == i_maxCu*1000]['T'].iloc[0]
adidataCu = pd.DataFrame()
adidataCu['t/tm']=xCu.apply(lambda x:x/t_maxCu)
adidataCu['i/im']=yCu.apply(lambda x:(x/(i_maxCu*1000))**2)

ax = plt.axes()
ax.plot(adidata['t/tm'], adidata['i/im'], color='blue',alpha=1,
        linewidth=0.1,linestyle="None",marker='^',
        markersize=3,markevery =0.01,Label='Cu+H2PO2')
ax.plot(adidataCu['t/tm'], adidataCu['i/im'], color='orange',alpha=1,
        linewidth=0.1,linestyle="None",marker='o',
        markersize=3,markevery =0.01,label="Cu")

ax.plot(ta,inst,color='purple')
ax.plot(ta,prog,color='gray')
ax.set(xlim=(0,5),ylim=(0,1.05),ylabel='(j/jm)$^{2}$',
       xlabel='t/tm', title= 'non-dimensional Plot')
ax.legend(loc='best', frameon=False, fontsize=10)
plt.show()
```


non-dimensional Plot
Cu+H2PO2
Cu
(j/jm)²
t/tm
0.0
0.2
0.4
0.6
0.8
1.0
0
1
2
3
4
5

Part 2: Supplementary information

The following contains the results commented on the research paper regarding the comparison of Cu and Cu-P electrocrystallization.

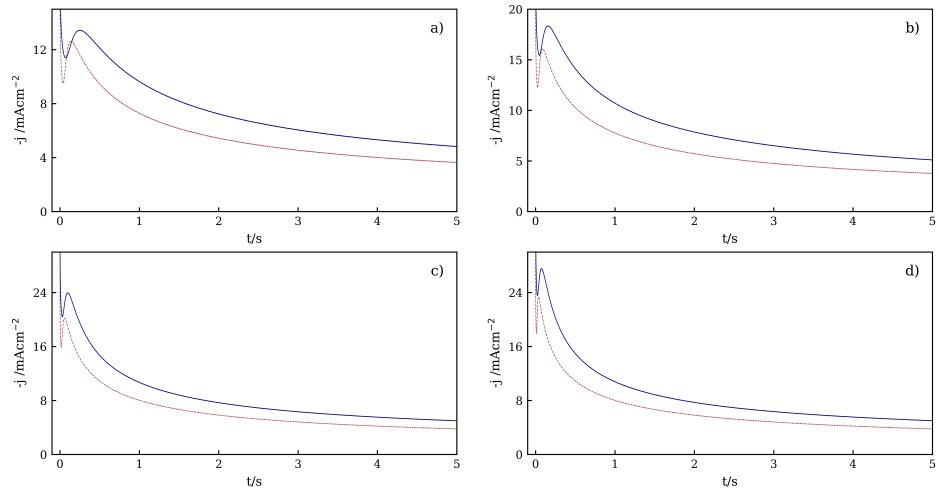


Figure S1. Current transients during reduction of Cu^{2+} on vitreous carbon from 0.04 M Cu^{2+} (· · ·) and 0.04 M Cu^{2+} + 0.04 M $H_2PO_2^-$ (–) in 1.5 M SO_4^{2-} acid aqueous solutions, at 220 (a), 240 (b), 260 (c) and 280 (d) mV.

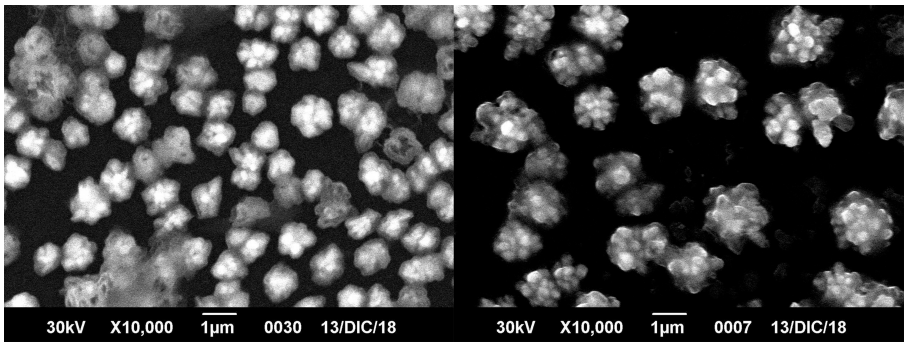


Figure S2. SEM images of the vitreous carbon surface obtained after electrodeposition of Cu from 0.04 M Cu^{2+} (left) and Cu-P from 0.04 M Cu^{2+} + 0.04 M hypophosphite (right), in aqueous 0.5 M H_2SO_4 + 1 M Na_2SO_4 solutions, at 190 mV overpotential during 180s. The saturation number densities of nuclei N_{sm} determined from the SEM images were $7.1 \cdot 10^7$ cm^{-2} (Cu) and $1.9 \cdot 10^7$ cm^{-2} (Cu-P).

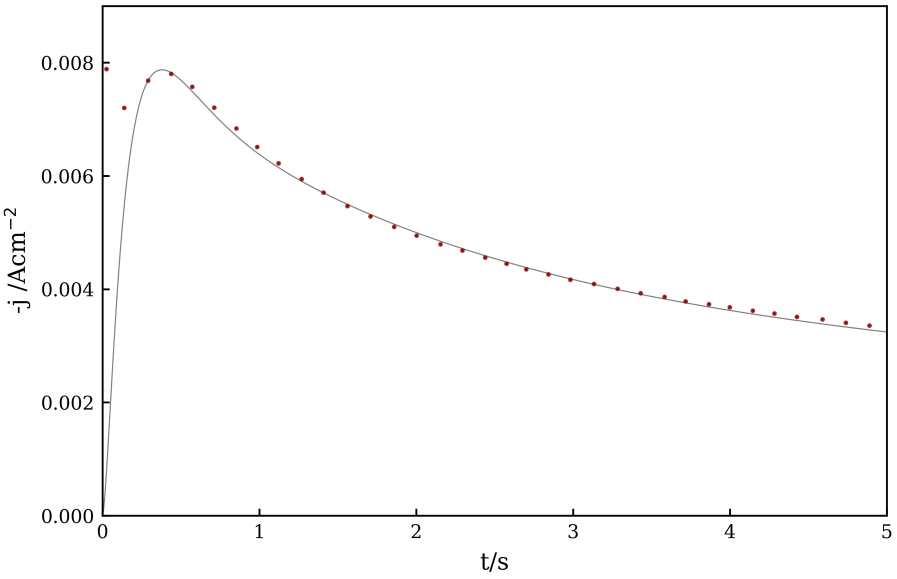


Figure S3. Current transient recorded during Cu deposition from 0.04 M Cu^{2+} solution at 190 mV (dots) and the non-linear fit of equation (S1) [44], to the experimental data (continuous line).

Zapryanova *et al.* [44] presented an expression to quantify the contribution of the electron transfer reaction $Cu^{2+} + e^- \rightarrow Cu^+$ with an exponential term $ae^{(-bt)}$:

$$j(t) = ae^{-bt} + \frac{FD^{1/2}c}{\sqrt{\pi t}}\left(1 - \exp\left\{-N_0\pi kD\left[t - \frac{(1-e^{-At})}{A}\right]\right\}\right) \qquad \text{(S1)}$$

The best fit parameters $A = 23.52\ s^{-1}$, $N_0 = 2.51{\cdot}10^6\ cm^{-2}$, $D = 2.77{\cdot}10^{-6}\ cm^2\ s^{-1}$, $a = 0.0237$ A cm^{-2} and $b = 4.0\ s^{-1}$ result in $N_{si} = 1.89{\cdot}10^6\ cm^{-2}$, *i.e.*, about 40 times lower than the corresponding $N_{sm} = 7.1{\cdot}10^7\ cm^{-2}$ value, cf. Fig. S2.

Reference:

[44] T. Zapryanova, A. Hrussanova, A. Milchev, *J. Electroanal. Chem.* 600 (2007) 311-317