

Supplementary Information

Electrodeposition study of the Cu-Zn-Mo system in citrate/sulfate medium

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The electrochemical behavior of the individual ions (Mo (VI), Zn (II) and Cu (II)) as well as for the ternary bath in the 2:2:1 molar ratio of

Mo:Zn:Cu (bath 3) on Pt was studied by cyclic voltammetry and are shown in Fig. S1.

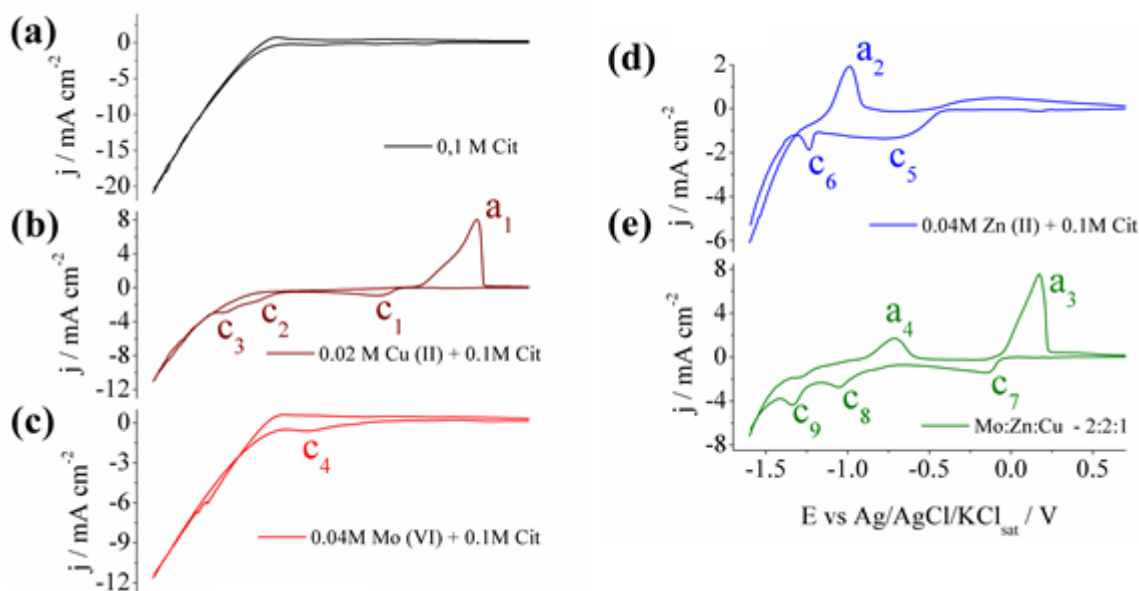


Figure S1. Cyclic voltammograms obtained on Pt in (a) 0.1 mol L⁻¹ of sodium citrate, (b) 20 mmol L⁻¹ of CuSO₄, (c) 40 mmol L⁻¹ of Na₂MoO₄, (d) 40 mmol L⁻¹ of ZnSO₄ and 0.1 mol L⁻¹ of citrate and (e) 2:2:1 molar ratio bath (40 Mo (VI) + 40 Zn (II) + 20 Cu (II) mmol L⁻¹).

The voltammogram of a solution without the metal ions (Cu (II), Zn (II) and Mo (VI), only with

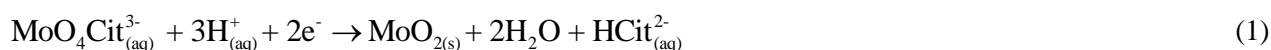
sodium citrate, is shown in Fig. 1Sa. The voltammogram shows no clear anode and cathode



peaks, only a high cathodic current in potentials after -1.0 V due to the hydrogen evolution reaction (HER).

In the voltammogram obtained for Cu (II) bath (Fig. S1b) the cathodic processes (c1, c2, and c3) in approximately -0.22, -0.96 and -1.15 V were attributed to the reduction of Cu (II) from different complexes formed between copper and citrate. At the concentration of citrate and pH used, the $[\text{CuH}_2\text{Cit}]^-$ and $[\text{Cu}_2\text{HCit}_2]^{3-}$ complexes are the predominant species, with low free Cu^{2+} ions. In the anodic branch, there is a shoulder followed by a peak (a1) in the region of potentials of 0.15 to 0.4 V both attributed to the dissolution of metallic copper deposited in the cathodic sweep¹.

In the voltammogram for Mo (VI) in citrate (Fig. S1c), two cathode processes can be noted, one



The cathodic sweep in the voltammogram for Zn (II) in citrate (Fig. S1d) shows a current plateau starting at -0.45 V (c5) and a peak at -1.25 V (c6). In the presence of citrate at pH 4.0 the ZnHCit^- complex is the major species and the processes c5 and c6 corresponding to the reduction of Zn (II) from this complex and the bare Zn^{2+} ions, respectively¹. In the anodic sweep, only a peak at -1.0 V attributed to the dissolution of electrodeposited Zn is observed.

Figure S1 shows the voltammogram obtained for the bath containing Mo(VI):Zn(II):Cu (II) in the 2:2:1 molar ratio (bath 5). The cathode peak at -0.15 V (c7) can be attributed to the deposition of Cu-rich species because it is in the same potential region of the c1 peak. In the cathodic sweep, two other peaks appear at -1.0 V (c8) and -1.3 V (c9), which compared to Fig. S1b and d, were attributed to Cu (II) reduction from the complexes formed between Cu (II) and citrate and the reduction of Zn (II), respectively. As for the reduction of Mo (VI), does not appear any definite peak in the presence of the three ions, however, a slight shoulder between the c7 and c8 peaks can be observed that is attributed the deposition of oxides/hydroxides of molybdenum. In the anodic scanning the peak of 0.16 V (a3) is attributed to the intermetallic phase oxidation containing in a higher proportion Cu with the other metals (Zn and Mo), since this process when compared to that of the voltammogram containing only Cu ions) (Fig. S1b) is shifted to more negative potentials. On the other hand, the

in the region of -0.6 V (c4) and another in -1.27 V. As metallic molybdenum can't be electrodeposited in solutions of its salts, only in the presence of certain metal ions that induce its co-deposition²⁻⁴, the process c4 is characteristic of the deposition of oxides/hydroxides of Mo. At the concentration of citrate and pH close to those used in this work, the Mo (VI) species are predominantly in the complexed form $[\text{MoO}_4\text{H}_4\text{Cit}]^{2-}$, and the proposed reaction for the formation of Mo oxides from this species is shown in the Eq. S1⁵ The small peak at -1.27 V was attributed to the evolution of hydrogen in profusion. During the anodic scan, no process is observed, this phenomenon is attributed to the passivating characteristics of the deposited molybdenum oxides.

anodic peak (a4) at -0.71 V was attributed to the dissolution of Zn-Cu intermetallic phases rich in Zn, since it appears close to the zinc oxidation region displaced to more positive potentials when compared to the Zn (II) oxidation peak only in citrate (Fig. S1d).

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