Arabian Journal of Chemical and Environmental Research

Vol. 13 Issue 1 (2026) 170–179

Impact of speciation on manganese electrochemistry in deep eutectic solvent medium based on choline chloride

M.S. Moutari [1] *, K. Adama [1], Soma F[1], S. Alassane [1], B. Moussa [1].

[1]*Laboratoire de Chimie Analytique, de Physique Spatiale et Energétique (L@CAPSE), UFR Sciences et Technologies), Université Norbert ZONGO (UNZ), Avenue Maurice Yaméogo (Rue de l'indépendance), BP 376 Koudougou, Burkina Faso*
**Email: mmahamadousambo@gmail.com*
Email: kindsadams@gmail.com
Email: alassorgho@yahoo.com

Received 25 November 2025, Revised 21 Feb 2026, Accepted 25 Feb 2026

Cited as: *Mahamadou Sambo Moutari, Kindo Adama, Fousséni Soma, Alassane Sorgho, Moussa Bougouma (2026) Impact of speciation on manganese electrochemistry in deep eutectic solvent medium based on choline chloride, Arab. J. Chem. Environ. Res. 13(1) (2026) 170-179*

Abstract

The electrochemical study of manganese in two different eutectic solvents, choline chloride-urea (ChCl-U) and choline chloride-oxalic acid dehydrate were studied on a glassy carbon electrode. The cyclic voltammograms recorded in the two media show differences from a kinetic point of view. Thus, the redox process of manganese occurs reversibly in the ChCl-Ac.Ox medium, while it is irreversible in the ChCl-U medium. The difference will be due to the presence of different Mn (II) species in the two media. The measurement of the UV-visible spectrum allows for the highlighting of the presence of a single species of manganese $[MnCl_4]^{2-}$ by the appearance of an absorption peak at 311 nm in ChCl- Ac.Ox medium and of two species of manganese at the peaks of 311 and 264 nm corresponding to $[MnCl_4]^{2-}$ and $[Mn(OH)_2Cl_4]^{2-}$in ChCl-U medium.

Keywords: pH of deep eutectic solvents, Lability of manganese complexes, Manganese.

---

*Corresponding author.
E-mail address: mmahamadousambo@gmail.com

1. Introduction

The growing interest in recent years in the use of new types of solvents commonly called deep eutectic solvents is explained by several of their properties. These solvents are easy to prepare, relatively biodegradable, cost-effective, and have a low ecological footprint (Choi *et al*.2011). Deep eutectic solvents (DES) were introduced in 2003 by Abbott *et al*.2003 with the choline chloride-urea mixture in a 1:2 stoichiometric ratio. In 2014, Smith *et al*.2014, generalized SEP as systems formed from a eutectic mixture of Lewis or Bronsted acids and bases. Among these solvents, type IV solvents are most used because they can form cationic metal complexes, ensuring a high concentration of metal ions near the electrode surface (Abbott *et al*., 2014). But also their high solubility of metals and good conductivity leads, several authors to use its solvent for the electrodeposition of manganese (Moutari *et al.* 2025, Guo et al. 2020), tellurium (Sorgho *et al*.2022), palladium (Beock *et al*., 2013, Lanzinger *et al. 2013*, Manolova *et al.* 2019, Soma *et al*.2020), silver (Rayée *et al*.2017, Sebastián *et al.* 2013, Sebastián *et al.* 2016), copper (Bernasconi *et al.* 2015, Obeten *et al.* 2017, *Sebastián et al*.2015), zinc (Abbott *et al.* 2011 , Bucko *et al.* 2019, Harati *et al.* 2012, Moutari *et al.* 2023, Vieira *et al.* 2015, Xueliang *et al.* 2016, Yang *et al.* 2014).

The electrochemical study of the behavior of different type IV solvents allows to highlight differences in behavior from a thermodynamic point of view (redox potential), kinetics of the deposit (nucleation and growth mechanism), or transport of matter (diffusion coefficient) and which could give information on the electroactivity of species in different solvents. However, very few studies have focused on the specificity of hydrogen bond donors (glycerol, urea, ethylene glycol, oxalic acid dihydrate) because of their high chloride ion content. The question of speciation seems to be neglected which nevertheless affects the dissolution of the metal by the formation of complexes based on chloride. The speciation study conducted by Rayée *et al*.2017, on silver allowed to conclude that the hydrogen bond donor has a weak influence on the electrochemical behavior of silver in deep eutectic solvents. Sorgho *et al*., (2022) did not reach the same conclusion, where they noted that the nature of the solvent strongly impacts the thermodynamics and the kinetics of electrodeposition of tellurium. Over 18,000 articles were gathered from Scopus on “Deep eutectic solvent” and 10,230 articles on “Manganese and Choline”, indicating the importance of these domains.

The present work consists of studying the specificity of manganese in choline chloride-urea (ChCl-U) and choline chloride-oxalic acid dihydrate (ChCl- Ac. Ox) media. The techniques used are cyclic voltammetry, chronoamperometry, UV-visible spectroscopy.

2. Experimental

2.1. Reagents and solution preparation

Choline chloride (ChCl) (Alfa Aesar, 98 %) purified by recrystallization from absolute ethanol (VWR Chemicals, NORMAPUR), filtered and dried under vacuum. Urea, oxalic acid dihydrate and the precursor salt $MnCl_2.4H_2O$ all (VWR Chemicals, NORMAPUR) were weighed and added directly without prior treatment, at the beginning of the measurements. The entire mixture precursor salt +ChCl-U is heated at 100 °C for 2H under magnetic stirring, in an oil bath, using a hot plate (IKA C-MAG HS7) equipped with a temperature sensor and a temperature control device (IKATRO N ETS-D5), until a homogeneous and transparent liquid is obtained. That of the mixture precursor salt+ ChCl- Ac. Ox is heated at 50 °C for 2H.

2.2. Experimental methods

Electrochemical experiments were carried out using a three-electrode system connected to an Autolab PGSTAT302N potentiostat (Metrohm). The measuring cell containing the electrolyte is made of glass. Before use, all glassware is cleaned with MilliQ water and dried in an oven. The working electrode is made of glassy carbon (BASi, geometric area = 0.0707 cm^2). It is polished with an alumina suspension (1.0 µm) - water on a porous neoprene mat (Struers), then subjected to two ultrasonic periods of 5 minutes and rinsed with Milli-Q water to eliminate all tracks of alumina, to finally dried with nitrogen. The counter-electrode is a platinum grid of the order of 3 cm^2 of electrochemically active surface. It is cleaned with a flame using a blowtorch of incandescent flame. A silver wire insulated in a capillary tube containing an electrolyte of a mixture of choline chloride-urea (ChCl-U) in 1:2 was used as a reference electrode. It was rinsed with water and dried with absorbent paper.

3. Results and discussion

3.1. Potentiodynamic study of the electrochemical behavior of manganese on glassy carbon electrode (ECV) in the presence of ChCl-U and ChCl- Ac. Ox

Figure 1A shows the 3^{rd} cycle of the cyclic voltammogram recorded on glassy carbon electrode in the ChCl-U mixture in the presence of 60 mmolal of $MnCl_2.4H_2O$. The responses related to the reduction of manganese are clearly visible and appear at the potentials of -1.50; -1.56 and -1.64 V, in the accessible potential window. The electrochemical phenomena highlighted through peaks C1, C2 and C3 on the orange voltammogram in Figure 1A could reflect the formation of several manganese species during cathodic scanning in the electrochemically accessible potential zone. The phenomena highlighted in C1, C2 and C3 could be translated by the following equations:

$$\mathrm{C1: Mn^{2+} + 2e^- \rightarrow Mn(0)} \quad (1)$$

$$\mathrm{C2: Mn^{2+} + 2OH^- \rightarrow Mn}\ (OH)_2 \quad (2)$$

$$\mathrm{C3: Mn(OH)_2 \rightarrow MnO} + H_2O \quad (3)$$

Deep eutectic solvents are known to form complexes with metal cations. Ligands such as chloride, urea, and residual water contained in DES or hydroxide ions (OH^-) could very well constitute the coordination sphere of the metal complex. This could lead to the formation of several types of compexes. The presence of hydroxides from the dissociation of residual water could lead to the formation of manganese-based complexes, which would explain the formation of C2 and C3 in accordance with the data (Kara *et al.*2020, Deng et al.2007). Figure 1B shows a cyclic voltammogram performed at 50 °C on a glassy carbon electrode in the mixture choline chloride- oxalic acid dihydrate (ChCl- Ac. Ox) in the presence of 25 mmolal of $MnCl_2.4H_2O$. A cathodic peak (C1) and an anodic peak (A1) respectively at potentials of +0.8 V and +0.6 V corresponding to the oxidation of Mn (0) and the reduction of Mn (II) according to equations (1) and (4) are observed:

$$\mathrm{C1: Mn^{2+} + 2e^- \rightarrow Mn(0)} \quad (1)$$

$$\mathrm{A1: Mn(0) \rightarrow Mn^{2+} + 2e^-} \quad (4)$$

The proximity of the oxidation and reduction potentials of manganese in the ChCl- Ac. Ox medium shows that the system ChCl-Ox.Ac + $MnCl_2.4H_2O$ on carbon electrode is fast.

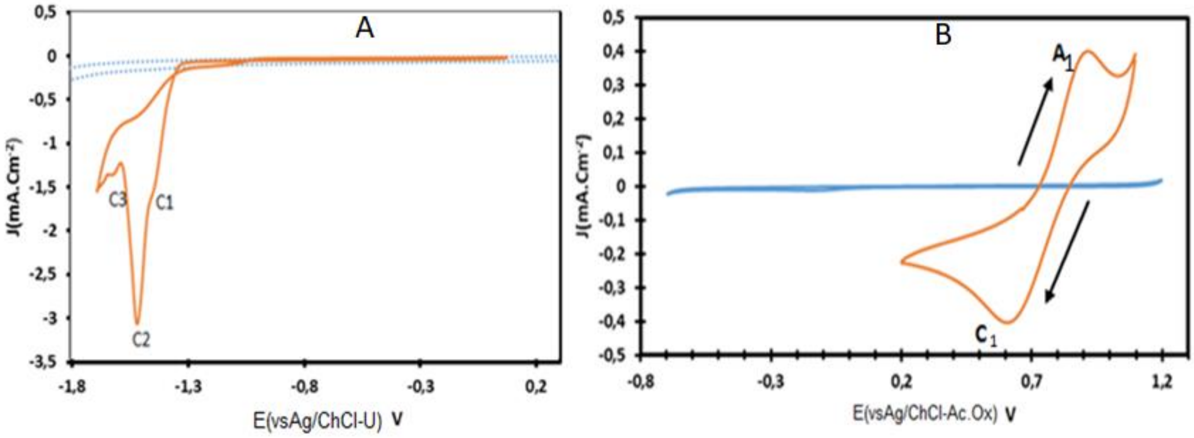

Figure 1 :*(A) cyclic voltammograms (3rd cycle), of the ChCl -U (1 :2) (dotted blue) and of the ChCl-U + 60 mmolal de $MnCl_2.4H_2O$ (orange line), T=100°C, v=10 $mV.s^{-1}$;(B) cyclic voltammograms (3rd cycle), of ChCl-U system (1 :2) (dotted blue) and of the ChCl-U + 25 mmolal of $MnCl_2.4H_2O$ (orange line), T=50°C, v=10 $mV.s^{-1}$; on a glassy carbon electrode.*

However, we note that in ChCl- Ox.Ac medium, the absence of peaks C2 and C3 and the appearance of a new peak A1 which would be linked to the oxidation of the manganese deposited on the surface of the electrode. Everything seems to believe that acidity (ChCl- Ox.Ac) favors the deposition of manganese much more than basicity (ChCl-U). Hypothesis which is confirmed by the potential of the deposition of manganese in ChCl- Ox.Ac medium which is more positive (0.6 V) than that of the ChCl-U medium (-1.50 V).

Figure 2A shows the cyclic voltammograms of the ChCl-U (1 :2) + 60 mmolal $MnCl_2.4H_2O$ system recorded on a glassy carbon electrode at different scanning speeds. Generally speaking, the scanning speed has a considerable influence on the electrochemistry of manganese in the medium. Indeed, the transition from low speed (10 $mV.s^{-1}$) to high speed (150 $mV.s^{-1}$) leads to a disturbance of the electrochemical phenomena reflected by the shape of the curve. Increasing the scanning speed promotes the deposition of metallic manganese, hence the disappearance of peaks C2 and C3 and the appearance of the anodic peak A1 at the potential of -1.1 V, corresponding to the oxidation of the deposited metallic manganese.

Figure 2B shows cyclic voltammograms obtained at different scanning speeds of the ChCl-Ac. Ox (1:1) + 25 mmolal $MnCl_2.4H_2O$. An increase in the intensity of the cathodic and anodic peaks is noted with a shift of the cathodic peak towards positive values. The intensities of the cathodic peaks vary linearly with the square root of the scanning speed, a phenomenon that is typical of kinetic control by diffusion (inset of Figure 2B)

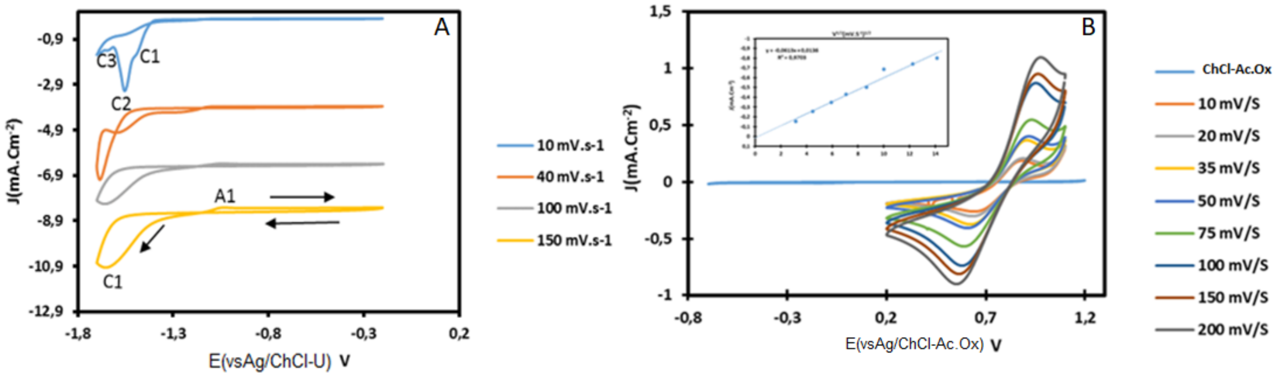

Figure 2B: *(A) cyclic voltammograms (3rd cycle) of the system ChCl-U (1 :2) + 60 mmolal $MnCl_2.4H_2O$, at different scanning speeds, T=100°C ; (B) cyclic voltammograms (3rd cycle) of the system ChCl-Ac. Ox (1:1) + 25 mmolal $MnCl_2.4H_2O$.*

3.3. Chronoamperometic study of the electrochemical behavior of manganese on a glassy carbon electrode

To better elucidate the nucleation and growth phenomenon highlighted, the appearance of the transient curves presented in Figure 3, provides information on the different phenomena occuring on the surface of the electrode. To record these transients for Figure 3a, the carbon electrode is subjected to a potential of 1.1 V (E_1) for 1 s, then to a second potential of 0.8 V (E_2) for 5 s before moving to the potential of 0.6 V (E_3) where a possible deposit is likely to occur. The transient obtained follows the

Cotrell model, which allows us to conclude on a rapid deposition of the species on the surface of the glassy carbon electrode. For the recording of transients for Figure 3b, the carbon electrode is subjected to a potential of -0.2 V (E_1) for 1 s, then to a second potential of -1.15 V (E_2) for 5 s before going towards the potentials where a possible deposit is likely to occur. This experiment informs us about the kinetics of deposition of growth mode by comparison with the theories established in the literature. Between -1.46 V and -1.50 V, all the transients recorded present the same upward current shapes which reach a maximum from which it decreases with time, except for the curve recorded at -1.50 V where the downward part occurs in two stages (Figure 3b). The curves obtained at different potentials show that the current density corresponding to the maximum current (j_{max}) increases as the potential tends towards negative values.

At the same time, the maximum time, corresponding decreases with the applied potential (Figure 3b and c). This means that the more cathodic potentials favor the formation of nuclei. However, all the recorded transients present the typical profile of nucleation and growth. When the potential varies between -1.52 V and -1.58 V (Figure 3c), a series of two increasing transitions are observed before reaching the maximum current in absolute values. Then a series of two decreasing transitions show that the nucleation and growth of manganese is influenced by other types of reactions attributable to the adsorption process of hydroxide ions OH^-, which constitutes a constraint on the growth of nuclei. Indeed, the study medium is basic choline chloride urea, therefore likely to release these OH^-ions into the electrolyte.

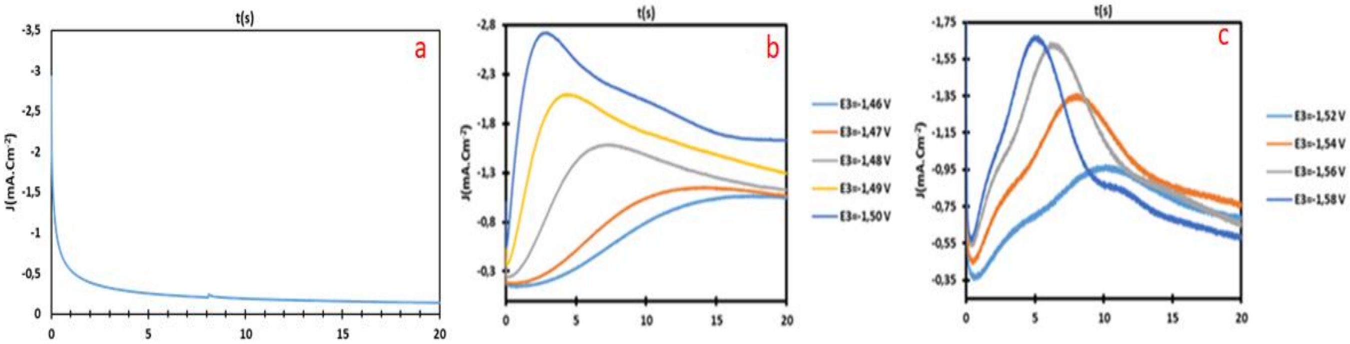

Figure 3: Transients recorded chronoamperometry in the system (a) ChCl-Ac.Ox+ 25 mmolal of $MnCl_2·4H_2O$ on a glassy carbon electrode at 50°C ; (b) ChCl-U + 60 mmolal of $MnCl_2·4H_2O$ on a glassy carbon electrode at 100°C.

3.4. Manganese speciation measurement in ChCl-Ac.Ox and ChCl-U medium

The introduction of the manganese salt (Figure 4) into the ChCl-Ac.Ox medium produces a colored solution under magnetic stirring at 50°C. In ChCl-U medium, the dissolution of the manganese salt produces a colorless solution under magnetic stirring at 100°C. This result allows us to conclude on the presence of different species in the two media. Figure 5 shows the UV-visible absorption spectrum recorded at 50°C in the ChCl-Ac.Ox medium and at 100°C in the ChCl-U medium.

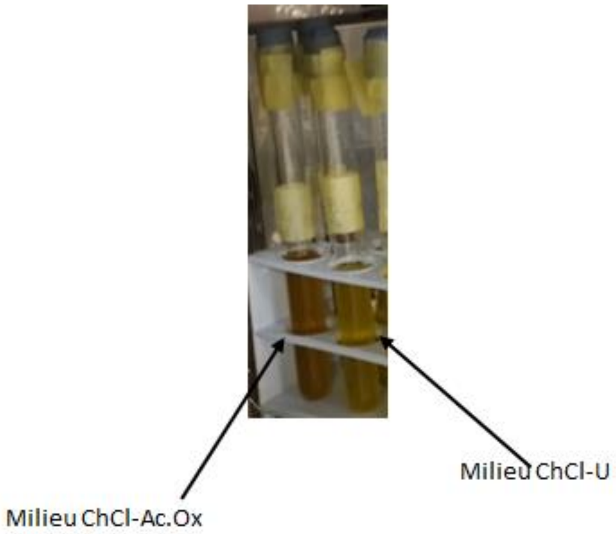

Figure 4: Solutions of $MnCl_2{\cdot}4H_2O$, 25 mmolal in ChCl-Ac.Ox medium and 60 mmolal in ChCl-U medium.

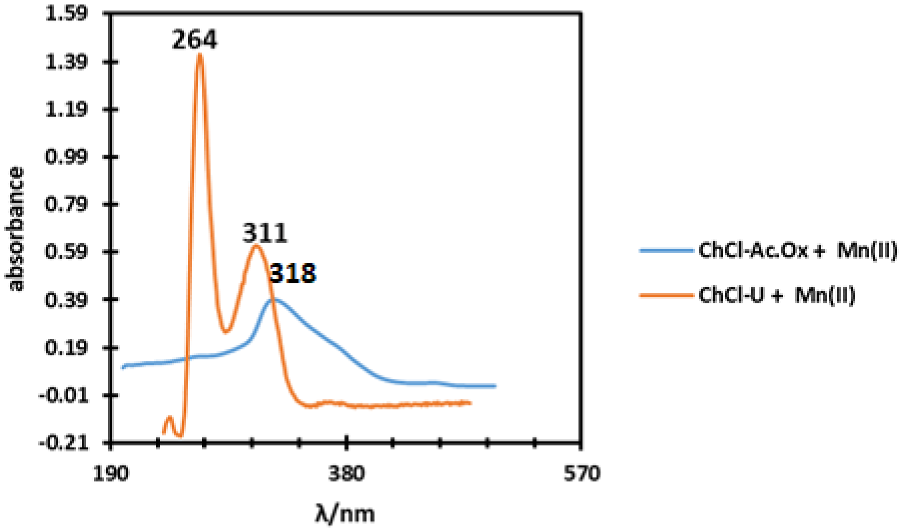

Figure 5: UV-Visible spectrum of the salt $MnCl_2.4H_2O$, in ChCl-Ac.Ox (blue) and ChCl-U (orange) medium.

The result of the measurements in the blue mixture of $MnCl_2{\cdot}4H_2O$ allows to highlight an absorption peak at the wavelength of 318 nm which would be attributed to the presence of the manganese chloride complex $[MnCl_4]^2$ (Hartley *et al.*, 2014). The spectrum measured in ChCl-U medium allows to highlight two absorption peaks at the wavelength of 264 and 311 nm which would be attributed to the presence of the manganese chloride complex $[MnCl_4]^{2-}$ and $[Mn(OH)_2Cl_4]^{2-}$ resulting from the adsorption of OH^- ions from the reduction of water molecules contained in the solvent.

Conclusion

Although both the solvents ChCl-U and ChCl-Ac.OX are highly (favorably) concentrated in chlorinated anion compounds, the speciation of Mn (II) differs in the two media. This result strongly suggests that the apparent pH is important in determining the speciation of manganese chloride, a compound prone to hydrolysis. Mn (II) being present under two different forms in the respective DES, its electrochemistry is markedly different in terms of thermodynamics and kinetics. More specifically, the latter is strongly dependent on the lability/inertness of the coordinating ligands. This study contributes to the understanding of the influence of the hydrogen bond donor in electrochemical processes conducted in DESs and reveals under which conditions the electrochemical recovery of manganese could be carried out in ChCl-U and ChCl- Ox.

References

Abbott. A.P., Barron. J. C., Frisch. G., Gurman. S., Ryder. K. S. and **Silva. A. F.** (2011), Double Layer Effects on Metal Nucleation in Deep Eutectic Solvents, *Phys. Chem*, 13, 10224–10231.

Abbott A.P., Capper G., Davies D. L., Rasheed R. K., and Tambyrajah V. (2003), « Novel solvent properties of choline chloride/urea mixtures », *Chem. Commun*, 1, 70-71, doi: 10.1039/b2a10714g.

Abbott A.P., Al-Barzinjy. A.A., Frisch. G, Harris. R.C., Hartley. J., Ryder. K.S. (2014), Speciation, physical and electrolytic properties of eutectic mixtures based on $CrCl_3 \cdot 6H_2O$ and urea, *Physical Chemistry Chemical Physics*., 16, 9047–9055.

Alassane S., Moussa B., Gael D.L., Julien V.S., Thomas D. (2022) Impact of speciation on the tellurium electrochemistry in choline chloride-based deep eutectic solvents, *Electrochemistry Communications*., 140,107327.

B€ock R., Lanzinger. G., Freudenberger. R., Mehner. T., Nickel. D., Scharf. I., Lampke T. (2013), Effect of additive and current mode on surface morphology of palladium films from a non-aqueous deep eutectic solution (DES), *J. Appl. Electrochem*., 43, 1207-1216, https://doi.org/10.1007/s10800-013-0608-4.

Bernasconi. R., Zebarjadi. M., Magagnin. L. (2015), Copper electrodeposition from a chloride free deep eutectic solvent, *J. Electroanal. Chem*, 758,163-169. https://doi.org/10.1016/j.jelechem.2015.10.024.

Bucko. M., Tomic. M. V., Maksimovic. M., Bajat. J. B. (2019), The importance of using hydrogen evolution inhibitor during the Zn and Zn-Mn electrodeposition from ethaline, *J. Serb.Chem. Soc*, 84, 1221-1234.

Choi Y. H., van Spronsen J, Dai Y, Verberme. M. (2011) “Are Natural Deep Eutectic Solvents the Missing Link in Understanding Cellular Metabolism and Physiology?” *Plant Physiol*., 4, 1701–1705.

Deng. M.J., Chen. P.Y., Sun. I.W. (2007), Electrochemical study and electrodeposition of manganese in the hydrophobic butylmethylpyrrolidinium bis((tri-fluoromethyl) sulfonyl) imide room-temperature ionic liquid, *Electrochim. Acta*, 53, 1931-1938.

Guo M.W., Sun C.B., Yang W.Q., Chen L., Lei H., Zhang Q.B. (2020), Sulphur-induced electrochemical synthesis of manganese nanoflakes from choline chloride/ethylene glycol-based deep eutectic solvent, *Electrochimica Acta*, 341, 136017.

Hartley. J. M., Chung-Man. Ip, Forrest. G. C. H., Singh. K., Gurman. S. J., Ryder. K. S., Abbott. A.P., and Frisch. G. (2014), EXAFS Study into the Speciation of Metal Salts Dissolved in Ionic Liquids and Deep Eutectic Solvents, *Inorg. Chem*, 53, 6280. doi.org/10.1021/ic500824r.

Harati. M., Love. D., Lau. W. M., Ding. Z. (2012), Preparation of crystalline zinc oxide films by one-step electrodeposition in Reline, *Materials Letters*, 2012, 89, 339–342.

Kara. Y., Boudinar. S., Kadri. A., Lepretre. J-C., Benbrahim. N., Chainet. E. (2020), Manganese and bismuth electrodeposition from a choline chloride based deep eutectic solvents, *Meet. Abstr.* MA2020-02, 3826, DOI: 10.1149/MA2020-02493826mtgabs.

Lanzinger G., B€ock. R., Freudenberger. R., Mehner T., Scharf I., Lampke T. (2013), Electrodeposition of palladium films from ionic liquid (IL) and deep eutectic solutions (DES): physicalechemical characterisation of non-aqueous electrolytes and surface morphology of palladium deposits, *Trans. IMF.*, 91, 133-140, https://doi.org/10.1179/0020296713Z.00000000097

Manolova M., B€ock. R. (2019), Electrodeposition of Pd from a deep eutectic solvent system: effect of additives and hydrodynamic conditions, *Trans. Inst. Met.Finish*, 97, 161-168, https://doi.org/10.1080/00202967.2019.1605755.

Moutari. M. S., Adama. K., Bougouma. M., Soma. F., Sorgho. A., *et al.* (2023), Temperature effect on zinc electrodeposition in choline chloride-urea deep eutectic solvent, *Mediterranean Journal of Chemistry*, 13, 228-239, http://dx.doi.org/10.13171/mjc02306161653bougouma

Moutari M.S., Kindo A., Fousséni S., Alassane. S., Moussa B., Giuseppina C., Philippe L. (2025) Electrodeposition of manganese in choline chloride-urea medium, J. Mater. Environ. Sci., 16(2), 371-381

Obeten. M. E., Ugi. B. U., Alobi. N. O. (2017), A review on electrochemical properties of choline chloride based eutectic solvent in mineral processing, *J. Appl. Sci. Environ. Manage*, 21 991-998. https://doi.org/10.104314/jasem.v21i5.29

Rayée Q., Doneux. T., Buess-Herman. C. (2017), Underpotential deposition of silver on gold from deep eutectic electrolytes, *Electrochimica Acta*, 237, 127–132

Sebastián P., Vallés. E., Gómez. E. (2013), First stages of silver electrodeposition in a deep eutectic solvent. Comparative behavior in aqueous medium, *Electrochim. Acta*, 112, 149–158, http://dx.doi.org/10.1016/j.electacta.2013.08.144

Sebastián P., Botello L.E., Vallés E., Gómez E., Palomar-Pardavé M., Scharifker B.R., Mostany J. (2016), Three-dimensional nucleation with diffusion controlled growth: A comparative study of electrochemical phase formation from aqueous and deep eutectic solvents, *J. Electroanal. Chem*, http://dx. doi.org/10.1016/j.jelechem.2016.12.014.

Sebastián P., Torralba E., Vallés E., Molina A., Gómez E. (2015), Advances in Copper Electrodeposition in Chloride Excess. A Theoretical and Experimental Approach, *Electrochimica Acta*, 164, 187-195. http://doi.org/10.1016/j.electacta.2015.02.206.

Soma F., Rayée Q., M. Bougouma, C. Baustert., C. Buess-Herman., Thomas Doneux (2020) Palladium electrochemistry in the choline chloride-urea deep eutectic solvent at gold and glassy carbon electrodes, *Electrochimica Acta, 345* ,136165.

Smith L., Abbott A. P., and Ryder. K. S. (2014), «Deep eutectic solvents (DESs) and their applications», *Chem. Rev*, 21, 11060-11082 doi: 10.1021/cr300162p.

Vieira. L., Schennach. R., Gollas. B. (2015), the Effect of the Electrode Material on the Electrodeposition of Zinc from Deep Eutectic Solvents, *Electrochimica Acta*, Http://Dx.Doi.Org/10.1016/j.Electacta.2015.11.030.

Xueliang. X., Xingli. Z., Xionggang. L., Changyuan. L.; Hongwei. C.; Qian. X.; Zhongfu. Z. (2016), Electrodeposition of Zn and CuZn alloy from ZnO/CuO precursors in deep eutectic solvent, *Applied Surface Science*, *385*, 481-489, https://doi.org/10.1016/j.apsusc.

Yang. H., Reddy. R.G. (2014), Electrochemical deposition of zinc from zinc oxide in 2:1 urea/choline chloride ionic liquid, *Electrochim. Acta*, 147, 513–519.

(2026) ; www.mocedes.org/ajcer