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## Electrochemical Characterization of Silver and Iron Ions in Choline Chloride-Ethylene Glycol DES Electrolyte

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Solar energy is growing to be an important source of renewable energy in the world, and the need of recycling processes to recover the strategic materials used for this technology are necessary. Ag may be recovered from photovoltaic cells using a Deep Eutectic Solvent (DES), by selectively dissolving Ag from the waste to Ag(I) by use of an Fe(III)/Fe(II) redox couple before the recovery of Ag metal by electrowinning. Electrochemical characterization of Ag and Fe ions in ethaline DES showed that Ag, Ag(I), Fe(II) and Fe(III) ions are stable, and the standard potentials of the relevant reactions are sufficiently far from one another for the electrochemical recovery of Ag. Diffusion coefficients were estimated to be  $1.77-4.16 \cdot 10^{-7} \text{ cm}^2/\text{s}$  and  $2.02-3.19 \cdot 10^{-7} \text{ cm}^2/\text{s}$  for Ag(I) and Fe(II) ions, respectively. High quality Ag deposits were obtained with Fe ions in the solution, and with water content up to 10 wt% in the DES electrolyte.

### Introduction

Solar energy is an important source of renewable energy in the world, and it is forecasted to grow significantly by 2050. The lifetime of solar cells is 25-30 years, and although the solar panels are producing zero-emission power during operation, it is necessary for the product to be sustainable throughout the entire life cycle. As such, the need of a recycling process to recover the strategic materials used in this technology is crucial. The PHOTORAMA project (PHOtovoltaic waste management – advanced Technologies of recOvery & recycling of secondary RAW MAterials from end-of-life modules) is proposing several new technology concepts to ensure effective recycling of end-of-life (EoL) modules and scrap, one of which is focusing on the recovery of Si and Ag metal from crystalline silicon (c-Si) photovoltaic (PV) technology cells.

Use of electrochemical methods to recover metals from different types of e-waste have several advantages compared to chemical methods like precipitation, cementation, adsorption, and liquid-liquid extraction, e.g., use of less solvent, reduced energy consumption, low environmental impact, and possibility of selectivity (1). However, e-waste is traditionally complex with respect to metal composition, consisting of both base and precious metals, and rare earth elements. This may result in possible problems if all are dissolved in the solution prior to electrowinning. Issues includes co-deposition, and when use of aqueous solutions, a quite narrow electrochemical window (1.23 V), limiting the metals that can be recovered. For this reason, new solvents with larger electrochemical windows are investigated to find solutions with better selectivity in both dissolution and electrowinning stage for e-waste recycling.

Deep Eutectic Solvents (DESs) have been proposed as a type of green solvent that could be used for metal recovery (2), and may be suitable for recycling of metals in EoL photovoltaic (PV) cells without introducing the typical high temperature processes or processes requiring strong acids and non-recyclable chemicals currently used for PV recycling (3). DESs are highly non-ideal mixtures of two biodegradable components associated with strong hydrogen bonding interactions, namely a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), mixed at eutectic composition. The resulting DES has a significantly lower melting point than the singular components, with operating temperatures as low as room temperature being possible. An eutectic mix of a halide salt (often choline chloride, ChCl) and the HBD, i.e., amides, carboxylic acids, alcohols, is the most common DES type (Type III) (2). Such a system is very adaptable and tunable for a variation of applications, mainly because the physical properties of the DES may vary significantly by changing the HBD (2).

A route to recover Si and Ag from EoL PV cells as well as scrap from PV manufacturing using a DES has been proposed and developed as part of the PHOTORAMA project. The suggested ionometallurgical route would integrate the leaching and electrowinning operations to recover the different metals, i.e., selective leaching of Ag and recover solid Si, followed by electrowinning of Ag. As such, the choice of DES should suit both operations, making sure the leachate is suitable to be used as the electrolyte for electrowinning of Ag. Compared to aqueous solutions and high temperature molten salts, DES solutions have high viscosity and low conductivity. The DES solution most referred to as the one with best inherent properties for electrowinning is the ethaline DES (4), comprising of choline chloride and ethylene glycol, most often in a 1:2 molar ratio.

In the leaching process, ionic complexes between silver from the waste and chloride ions are formed in the DES by the use of an oxidizing agent. The oxidizing agent should be electrochemically and chemically stable in the DES, and it should not interfere with the Ag deposition reaction. Compared to the Ag(I)/Ag redox-system (5-6), the redox standard potential of Fe(III)/Fe(II) in ethaline is significantly higher in the ethaline system (7), i.e., 0.25 V for Fe(III)/Fe(II) and -0.1 V for Ag(I)/Ag(0) vs the  $\text{Fe}(\text{CN})_6^{3-/4-}$  reference couple. The difference of approximately 0.35 V makes the leaching process and the recovery of the oxidant at the anode during electrowinning feasible. As such, Fe(III) chloride may be a suitable oxidizing agent for the recovery route as long as Fe does not co-deposit with Ag. In an ideal solution after leaching, only Ag(I) and Fe(II) ions will be present in the electrolyte. However, the iron species may affect the Ag electrowinning process, both Fe(II) ions generated during the leaching process and the excess of Fe(III) ions in case the leaching is not 100 % effective. By choosing commercial  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as the oxidant, water is introduced to the system, and as DES solvents have high hygroscopicity (8) water may additionally be introduced from the air. The presence of water in the DES electrolyte may also reduce the electrochemical window of the DES, or due to new complexation of the electroactive species, affect the electrodeposition of silver.

In this work, ethaline solutions with Ag(I), Fe(II) and Fe(III) added as chlorides were investigated electrochemically by cyclic voltammetry and chronoamperometry. Moreover, Ag deposits were obtained by electrolysis at potentiostatic and galvanostatic conditions. The quality of the metal deposits was investigated by SEM-EDS. The goal was to characterize the Ag(I)/Ag and Fe(III)/Fe(II) electrochemical systems, and to understand

how the presence of iron species and water may affect the electrowinning of silver in a proposed recycling scheme for PV cells.

## Experimental

The ethaline DES was prepared by mixing choline chloride (Sigma Aldrich,  $\geq 98\%$ ) and ethylene glycol (Acros Organics, 99+%) in a 1:2 ChCl:EG molar ratio at 60 °C until a clear liquid was formed. After cooling, the DES was mixed with AgCl (Sigma Aldrich,  $\geq 99.95\%$ ), FeCl<sub>2</sub> (Sigma Aldrich, 99.5%) and/or FeCl<sub>3</sub>·6H<sub>2</sub>O (Sigma Aldrich, 97.0-102.0%) at 60 °C to obtain the targeted concentrations for the model solutions (10, 25, 50 or 100 mM). Distilled water was added to some of the solutions. The water content in the DES samples was investigated using volumetric Karl Fisher (KF) titration, while the contents of Ag and Fe were measured by ICP-MS. It should be noted that ICP-MS analysis of silver from the DES solution can be difficult to perform accurately since silver chloride precipitates when the solution is diluted with other aqueous solvents than DES (e.g., with HCl), because of a lower solubility of silver chloride in these solvents (anti-solvent crystallization). For the Ag analysis the uncertainty could be  $\pm 30\%$ .

The electrochemical experiments were conducted at 60 °C using a typical 3-electrode arrangement. A stable reference system was constructed using a Pyrex tube closed with a porous glass frit containing AgCl dissolved in the ethaline with an Ag wire immersed, establishing the Ag(I)/Ag reference system and also allowing the electrical connection. A Pt spiral was used as counter electrode, also immersed in a Pyrex tube closed with a porous glass frit containing the same electrolyte as in the main electrochemical cell. Different working electrodes were used. Pt (0.5 mm wire) and glassy carbon (GC, 3 mm rod) were used to ensure the electrochemical signals reflected the desired electrochemical reactions, e.g., alloying between Ag and Pt may affect the voltammograms. Additionally, Pt is known to catalyze the hydrogen reaction, limiting the electrochemical window as this is one of the possible cathodic reactions (9). Deposition on Ag (1 mm wire) was done to evaluate if there were any significant differences of silver quality when depositing silver on silver, and deposition on 316L stainless steel (3x5 mm sheet) was included as a probable cathode material in the suggested recycling process.

Electrochemical evaluations were done using a PAR4000+ Potentiostat Galvanostat equipped with the Versastudio Software. Electrochemical investigations included cyclic voltammetry (CV), chronoamperometry (CA), and deposition of Ag using constant current and potential. The CV curves were obtained using Pt or GC as substrates with scan rates varying in the 10-500 mV/s range. CA measurements were done by stepping the potential from the open circuit potential (OCP). Ag deposits were obtained by choosing suitable potentials and/or current densities based on the CA results obtained. The deposits were rinsed in ethanol solution, with or without an ultrasonic bath depending on adherence between the substrate and deposited metal (for bad adhering deposits, ultrasonic bath resulted in the deposit being removed, collecting in the bottom of the beaker). The deposits were subsequently investigated by using a Scanning Electron Microscope Hitachi model S3400N equipped with an Energy Dispersive X-ray Spectroscopy detector (EDS, Oxford Instruments, UK).

## Results and Discussion

### Ag(I)/Ag system

Ag(I) and Ag(0) were found to be stable in the DES solution. In the CVs obtained for the 10 mM AgCl solutions (Figure 1a), the electrochemical signals obtained are clearly observed (A/A') far from the electrochemical limit of the ethaline DES (B/B'). The cathodic limit of the DES (B) is very different for GC and Pt, likely due to the catalyzation of hydrogen evolution (9) on Pt, but still far from the Ag(I)/Ag electrochemical couple A/A'. By comparing the voltammetric curves obtained with the GC and Pt electrodes, the nucleation overpotential on GC compared to Pt is almost 300 mV. The potential needed for the initial formation of Ag nuclei is significantly higher than what is needed for Ag growth on GC compared to Pt, reflecting the importance of the surface of the electrode when depositing on a foreign substrate. When increasing the concentration of Ag(I) in the solution to 50 mM, the re-dissolution reaction of the deposited Ag on GC was affected, and additional peaks/broadening of the electrochemical signal were observed (marked A'' in Figure 1b, also observed for the 25 mM solution). Besides, a typical cross-over due to the nucleation overpotential was clearly obtained. Due to the observations on GC, most of the following results related to Ag(I)/Ag system is presented using the Pt electrode, as no additional peaks were observed on this electrode due to possible alloying.

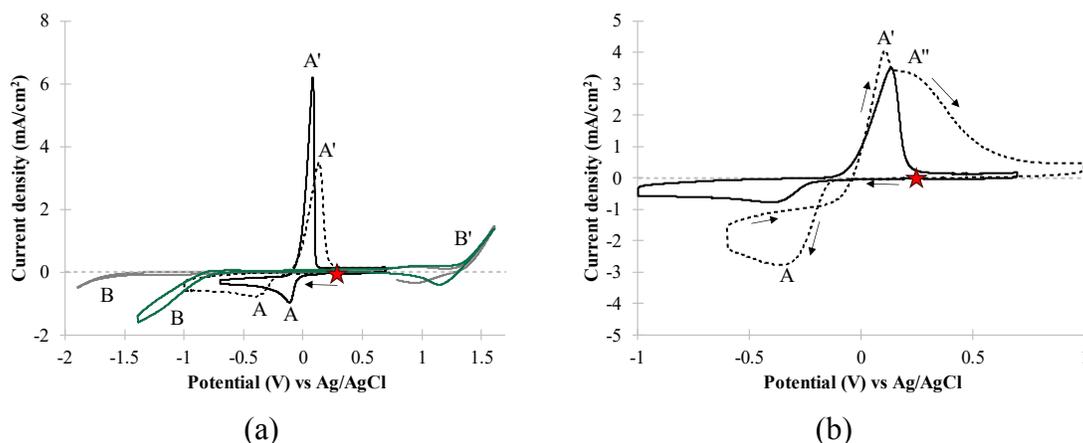


Figure 1. CVs obtained with a scan rate of 200 mV/s from model system with Ag(I) in 1ChCl:2EG. (a) Comparison between the curves obtained on Pt (black solid line) and GC (black dashed line) electrodes with 10 mM Ag(I), and the pure system on GC (grey solid line) and Pt (green solid line). (b) Comparison between the CV curves obtained on 10 mM (solid line) and 50 mM Ag(I) (dashed line) solutions on the GC substrate. The start potentials of the scans are marked with a red star.

CVs at different sweep rates were obtained using Pt (Figure 2a). Plots of the anodic and cathodic peak potentials versus the logarithm of the sweep rate showed that the Ag(I)/Ag system could be considered reversible at scan rates  $\leq 100$  mV (Figure 2b). The  $E^\circ$  potential can be estimated using Equation 1 for insoluble-soluble systems (10), where  $E_{pc}$  (V) is the cathodic peak potential,  $n$  is the number of electrons transferred in the redox reaction,  $F$  is the Faraday constant (C/mol),  $c_0$  is the concentration of electroactive species in the bulk solution (mol/cm<sup>3</sup>),  $R$  is the gas constant (J/K/mol), and  $T$  is the temperature (K).  $E^\circ$  was calculated as 0.26 V vs Ag/AgCl.

$$E^o = E_{pc} - 2.3 \frac{RT}{nF} \log c_0 + 0.849 \frac{RT}{nF} \quad [1]$$

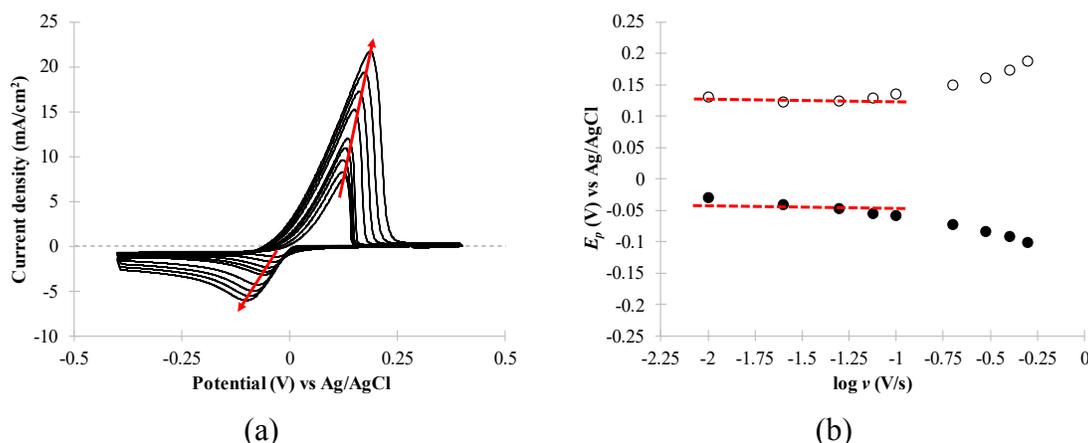


Figure 2. (a) CVs obtained in model systems with 50 mM Ag(I) in 1ChCl:2EG, on a Pt electrode at 10-500 mV/s scan rates, with arrows indicating higher scan rate. (b) Anodic (hollowed dots) and cathodic (filled dots) peak potential values versus the logarithm of the sweep rates extracted from the CV curves in (a).

The Berzins-Delahay equation (Equation 2) could be used to determine the diffusion coefficient of the Ag(I) electroactive species with the CV data for the reversible conditions (11), where  $i_p$  is the cathodic peak current density ( $A/cm^2$ ),  $D$  the diffusion coefficient ( $cm^2/s$ ), and  $v$  is the scan rate (V/s). The relevant plot is presented in Figure 3.

$$i_p = 0.61 \cdot (nF)^{3/2} \cdot c_0 \cdot \left(\frac{Dv}{RT}\right)^{1/2} \quad [2]$$

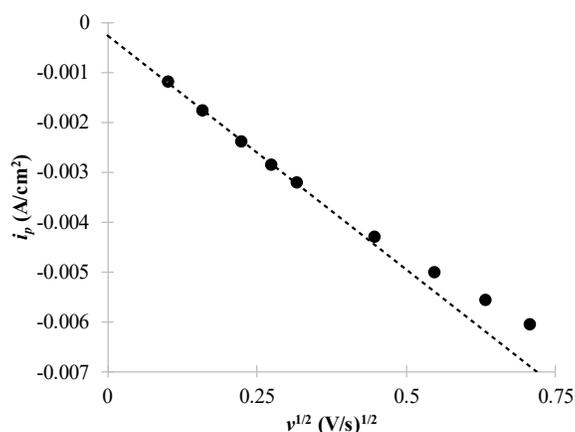


Figure 3. Verification of Berzins-Delahay equation. Cathodic peak current density vs square root of the scan rate obtained from the 50 mM Ag(I) in 1ChCl:2EG on a Pt substrate.

The diffusion coefficient for Ag(I) on Pt was calculated to  $4.16 \cdot 10^{-7} cm^2/s$ . Despite the nucleation overpotential on GC (Figure 1) the deposition itself appeared unaffected and was also reversible at slow scan rates, similar as for Pt. The diffusion coefficients should be similar for the same species in the solution, but the estimated diffusion coefficient using GC was somewhat smaller than on Pt ( $1.77 \cdot 10^{-7} cm^2/s$ ). This may be due to the nucleation

effect in the CV curves, or to the different electric double layer structure on both substrates, as reported by Costa et al. (12). The values obtained on each of the electrode materials at the different concentration of Ag(I) electroactive species studied, i.e., 10 and 50 mM, were similar, and within the assumed error of the technique. The values obtained are in agreement with those reported in the literature (5), and significantly lower than those obtained in aqueous solutions (13), which is mainly due to the higher viscosity of DES solvents.

An example of Ag deposit obtained on Pt in the 50 mM Ag(I) solution is presented in Figure 4. The Ag particles have a well-defined shape, appearing to be as truncated octahedrons. It seems like that Ag preferred to grow into large particles instead of having more nucleation sites and forming a dense, fine-grained layer covering the entire electrode surface. Some impurities were identified during the EDS analysis: C, O or Cl probably stemming from DES electrolyte remains despite being rinsed in ethanol with an ultrasonic bath. The silver deposited on GC was not analyzed with SEM due to bad adherence; most of the deposited metal fell off the electrode when removing it from the electrolyte bath.

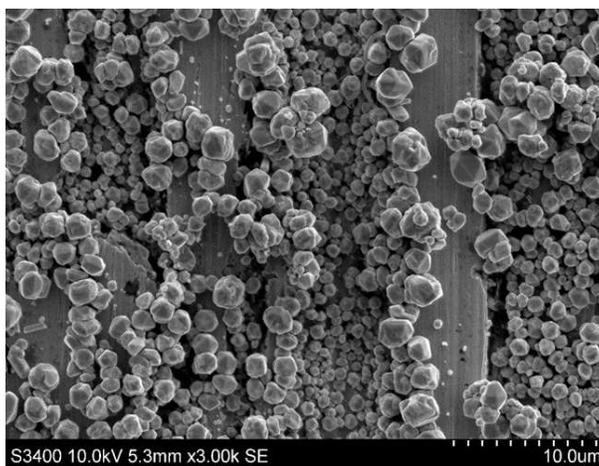


Figure 4. Example of Ag deposits obtained on Pt in the DES solutions with 50 mM Ag(I) added as AgCl. 15 min constant potential deposition at  $-0.05$  V vs Ag/AgCl under stirring of the electrolyte.

### Fe(III)/Fe(II) system

CVs on Pt and GC electrode for a solution with 50 mM dissolved Fe(II) are presented in Figure 5a. Due to the catalytic effect of Pt on the hydrogen evolution reaction (B), the cathodic limit obtained on the Pt electrode was lower than that on the GC substrate (also observed in Figure 1a for the pure DES systems). The decomposition product could be easily recognized by gas evolution, as reported in the literature (9). No iron deposition reactions were observed within the electrochemical window of the DES electrolyte. However, a small electrochemical signal was observed in the reverse scan in Figure 5a (B'') on the GC electrode at  $\sim -0.4$  vs AgCl/Ag. It was not possible to detect any new electrochemical signals in the cathodic scan before the decomposition of the DES electrolyte paired to this signal, indicating that possible iron deposition occurs at or very close to the cathodic limit of the DES. This is in agreement with previous reported results (14). The Fe(III)/Fe(II) peaks (C/C') do not change for the two electrodes, likely because

the soluble-soluble reaction is less dependent on the substrate than the soluble-insoluble reaction observed for the Ag(I)/Ag system.

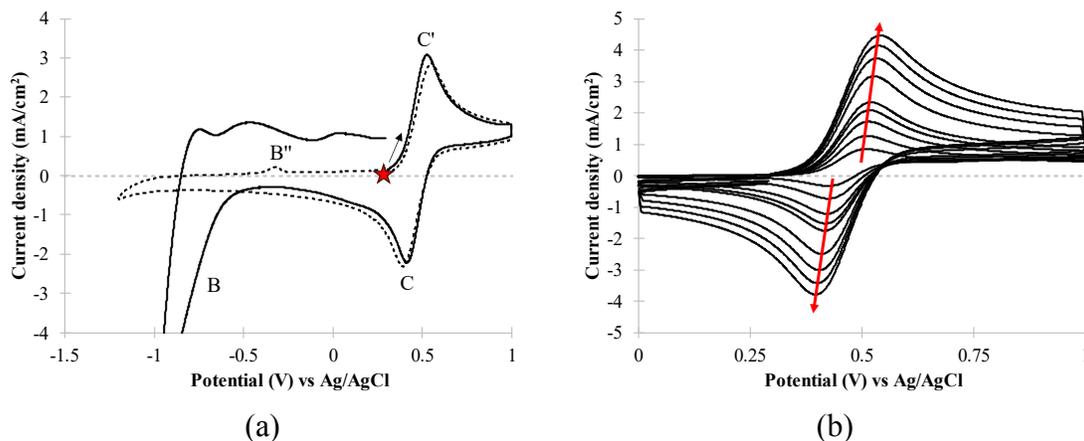


Figure 5. CVs obtained from a model system with 50 mM Fe(II) added as FeCl<sub>2</sub> in 1ChCl:2EG. (a) Comparison between the Pt (solid line) and GC (dotted line) electrodes using 200 mV/s scan rate. (b) CVs obtained at 10-500 mV/s scan rates on Pt, with arrows indicating higher scan rate.

This results in Fe(II) and Fe(III) ions as stable species in the DES electrolyte (C/C'), while metallic Fe may not be stable leading to spontaneous decomposition of the electrolyte, as Gamarra et. al. (15) managed to deposit flaky Fe on GC already at -0.95 V vs Ag/AgCl. Similar as for Ag, CV curves of the Fe(III)/Fe(II) system (Figure 5b) obtained showed that the system is reversible at lower scan rates. Assuming that the diffusion coefficient of both Fe(II) and Fe(III) are similar, the half wave potential,  $E_{1/2}$ , can be considered equal to the standard potential of the Fe(III)/Fe(II) system, and estimated by using Equation 3 (16). The value obtained was 0.47 V vs Ag/AgCl on both Pt and GC.

$$E_{1/2} = E^o = \frac{E_{pc} + E_{pa}}{2} \quad [3]$$

The Randles-Ševčík equation (Equation 4) can be used to estimate the diffusion coefficient of the Fe(II) electroactive species from the CV data (anodic current density,  $i_p$ , of signal C') where the system is reversible (17-18), resulting in a value of  $3.19 \cdot 10^{-7} \text{ cm}^2/\text{s}$  on Pt and  $2.02 \cdot 10^{-7} \text{ cm}^2/\text{s}$  on GC. The values are in the same range as those obtained for Ag(I) ions.

$$i_p = 0.446 \cdot (nF)^{3/2} \cdot c_0 \cdot \left(\frac{Dv}{RT}\right)^{1/2} \quad [4]$$

### Effect of Iron Speciation on Silver Deposition

Based on the investigations of the single systems with Ag(I) and Fe(II) by identifying the electrochemical reactions and potentials, the proposed recycling scheme using Fe(III) to dissolve Ag from the waste to Ag(I) should be feasible. The resulting leachate should have Ag(I) and Fe(II) ions, ideally resulting in no competing reactions on the cathode during the electrowinning of Ag. The diffusion coefficients of the relevant ions are also similar, and as Ag(I) and Fe(II) should be present in the same concentrations, a proposed electrowinning process should require approximately the same anode and cathode electroactive areas to avoid decomposition of the DES electrolyte. However, there might

be excess Fe(III) ions after the leaching process. The complexation of the Ag(I) when Fe(II) and Fe(III) ions are present in the DES may change, thus affecting the silver electrodeposition reaction. Additionally, the presence of Fe(III) ions will result in electrochemical losses during the cathodic recovery of Ag.

CVs obtained in model solutions containing 50 mM Ag(I), and 50 mM Fe(II) or Fe(III) ions, are presented in Figure 6a. The open circuit potential value (OCP, which is the potential value at zero current) could be a way to predict the efficiency of the leaching process, indicating the presence/absence of excess Fe(III). The quasi steady-state  $i$ - $E$  curve (Figure 6b) was obtained using the potential dependent current values of the CA curves by extracting the stable current after  $\sim 30$  s at each potential. As expected, the Faradaic losses when Fe(III) ions are present are clearly visible. The limiting cathodic current for Ag(I) reduction, the stabilized plateau value seen at potentials  $<0$  V, is approximately 0.8 and 1.6 mA/cm<sup>2</sup> with equimolar Fe(II) or Fe(III) present. When Fe(III) is present, an additional plateau is observed at potentials  $>0$  V, which is the current that must be overcome to start cathodic deposition of Ag.

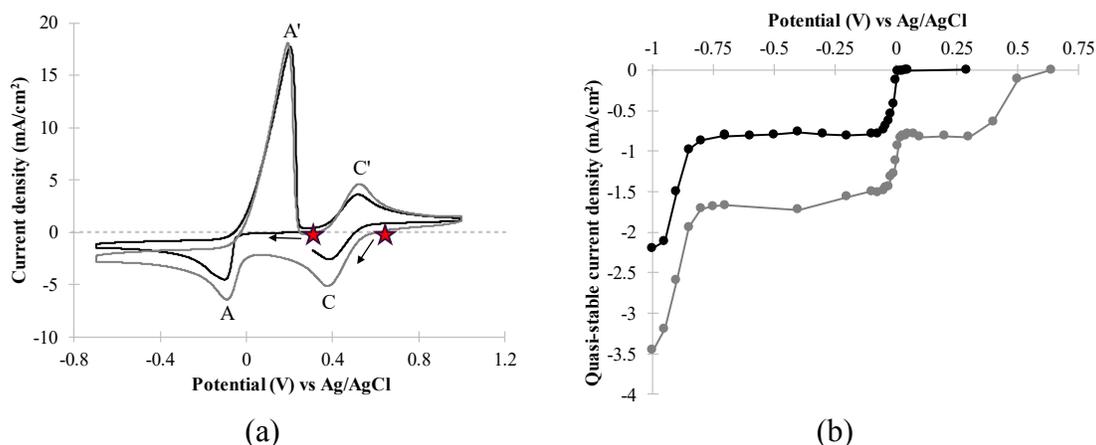


Figure 6. Evaluations on Pt electrode using 50 mM Ag(I) dissolved as AgCl in 1ChCl:2EG, with equimolar Fe(II) ions (black) or Fe(III) ions (grey), added as chlorides. (a) CVs obtained at 200 mV/s. The OCP values obtained on each case are marked with red stars. (b) Quasi steady-state  $i$ - $E$  curves obtained from CA measurements.

As such, at equimolar Ag(I) and Fe(III) contents, the current efficiency (CE) for the Ag deposition reaction is approximately 50 %. This is because both reactions are involving 1 electron exchange, and the diffusion coefficients of both Ag(I) and Fe(III) electroactive species are similar. In the proposed recycling process, the excess of oxidant Fe(III) in the leaching step must be minimized, so the Ag recovery has a maximum throughput. SEM images of Ag deposited on Pt for the two outlier cases are presented in Figure 7, showing nice, dense layers of Ag particles on the electrode surface. The silver has grown as truncated octahedrons, looking similar independently of the Fe speciation, and no Fe was detected in the EDS point analysis (summarized in Table I for all solutions). Good adhesion was observed in both cases, as cleaning using ultrasonic bath was possible without removing any of the deposited metal. Compared to the deposits in the pure Ag(I) system (Figure 4), the morphology is almost identical, but the Ag appeared to grow more evenly on the surface in the cases with Fe present (although this may be caused by other effects, like surface preparation and deposition time). Similar results were obtained when investigating other substrates; high quality deposits were obtained on Ag in addition to Pt,

while silver deposited on 316L stainless steel appeared of the same quality but did not adhere as easily (ultrasonic bath resulted in removal of metal from substrate). It appears that when Ag(I), Fe(II) and Fe(III) ions are in the DES solution, no difference is observed in the resulting silver deposit quality for the three substrates Pt, Ag, and 316L.

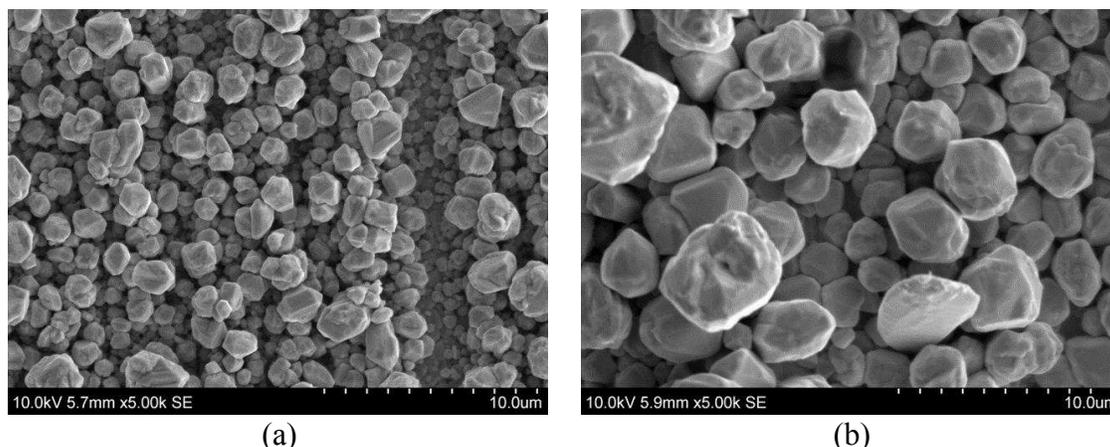


Figure 7. Ag deposits obtained in the DES solutions with 50 mM Ag(I) on Pt at galvanostatic conditions under stirring of the electrolyte. (a) +50 mM Fe(II), 15 minutes deposition time at  $1.15 \text{ mA/cm}^2$ , and (b) +50 mM Fe(III), 30 minutes deposition time at  $1.98 \text{ mA/cm}^2$ .

#### Effect of the Presence of Water in the DES Electrolyte

The Ag(I)/Ag and Fe(III)/Fe(II) electrochemical system have also been investigated in the presence of water. The DES after leaching may have additional water not corresponding to the crystal water from the  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  oxidant. The ChCl might retain some water before mixing, and the ethaline DES is known to be hygroscopic. The content of water in model solutions was analyzed by KF and the results are presented in Figure 8. Pure DES solutions had  $\sim 0.4 \text{ wt}\%$  water, with just a small increase when dissolving the  $\text{FeCl}_2$  salt. An increase to  $1.08 \text{ wt}\%$  is approximately corresponding to the crystal water amount in the solution where  $50 \text{ mM FeCl}_3 \cdot 6\text{H}_2\text{O}$  is dissolved.

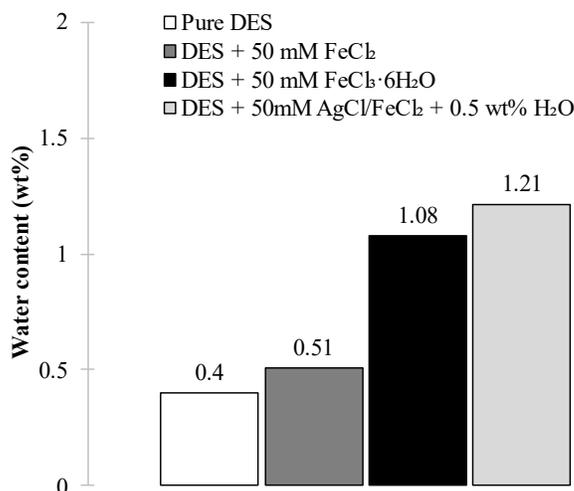


Figure 8. Water content in DES model systems as measured by Karl Fischer titration (average of 2 parallels, standard deviation 0-0.03 wt%) after five days storage.

The KF results show that at least 1 wt% water is present when leaching of Ag-containing waste by  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  leading to 50 mM Ag(I) and Fe(II) in the DES solution, whereas the model solutions presented previously only had about half of this water present since the Fe(II) was added directly as  $\text{FeCl}_2$ . The presence of water or crystal water in DES systems have previously been shown by Valverde et. al. to shift electrochemical systems to more positive potential values, e.g., in the Cu(I)/Cu(0) system (19). This was also observed in the case of Ag(I)/Ag system when adding water in equivalent amount as would have been added through the crystal water from the oxidant (1.21 wt% water measured, see Figure 8). This may be explained by the decrease in electrolyte viscosity upon addition of water (19). No difference was observed when investigating the quality of the obtained Ag deposits under these conditions, i.e., nice, dense layers of Ag in form of octahedrons were deposited on Pt, Ag and 316L stainless steel without any Fe detected.

The electrochemical window of the DES itself has been shown to not be affected with water contents up to at least 15 wt% (19). A comparison between the CVs obtained in the pure DES system and with 5, 10 and 15 wt% water is presented in Figure 9 using the Pt electrode. The steeper slope for the anodic/cathodic decomposition reactions shows the improved conductivity upon water additions, and confirming that no significant difference is observed for the decomposition reactions of the DES electrolyte.

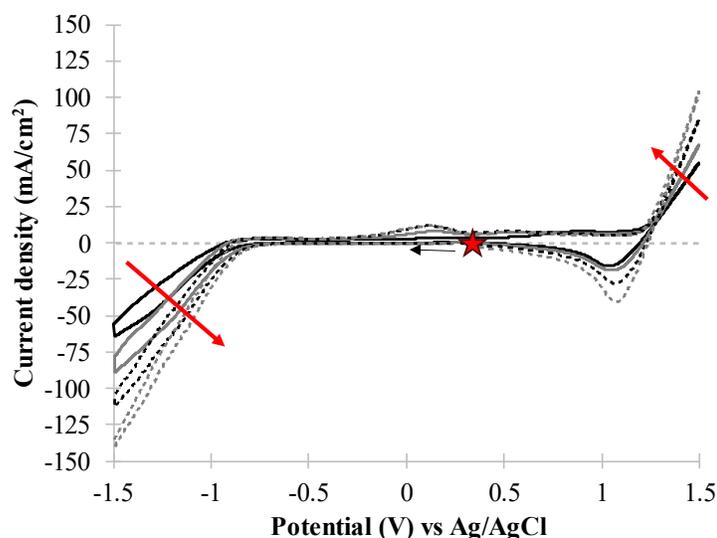


Figure 9. CV curves obtained with 200 mV/s on a Pt electrode in pure 1ChCl:2EG, and with 5, 10 and 15 wt% water additions. The red arrows indicate increase in water content. The start potential of the scan (OCP) towards the cathodic direction is marked with a red star.

10 wt% water content has been suggested as a value where the ratio between  $\text{Ch}^+$ ,  $\text{Cl}^-$ , EG and water may still be suitable for metal dissolution and possible electrochemical recovery (20). 100 mM Ag(I) and Fe(II) solutions in the ethaline electrolyte were investigated before and after adding 10 wt%  $\text{H}_2\text{O}$ . The addition of water implies a net reduction of the bulk concentration of the metal ions. Despite this concentration reduction, the CV curves (Figure 10a) clearly show higher electrochemical peak currents and a less negative deposition potential. This is also evident in the quasi-steady state  $i$ - $E$  curves in Figure 10b where a large increase in limiting current for the Ag deposition is observed and is due to the improved electrochemical properties in the electrolyte with water. This could

be utilized in a recycling scheme as higher currents could be applied, given no issues with metal quality and stability of electrolyte.

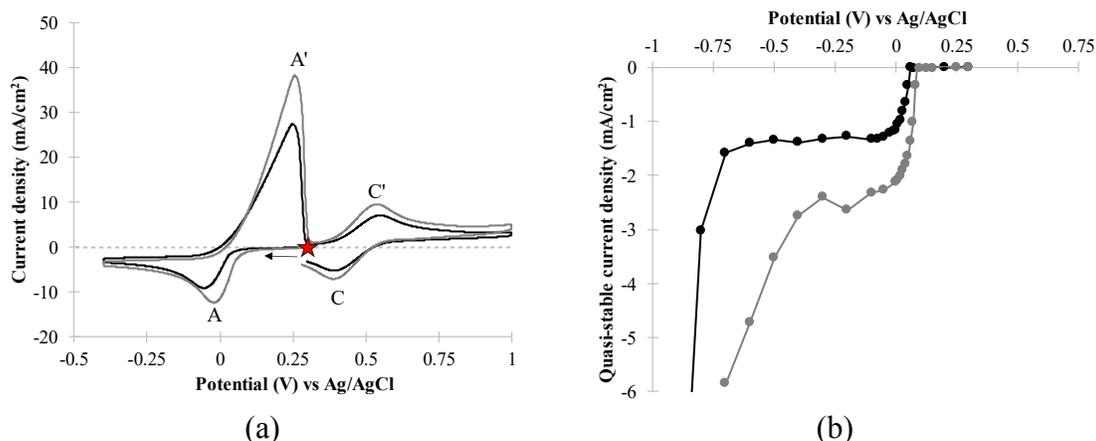


Figure 10. Evaluations on Pt in a 100 mM Ag(I) and Fe(II) solution in 1ChCl:2EG before (black) and after (grey) adding 10 wt% water. (a) CVs obtained with scan rate 200 mV/s. The start potential of the scan (OCP) is marked with a red star. (b) Quasi-steady state  $i$ - $E$  curves obtained from CA measurements.

The  $i$ - $E$  curve in Figure 10b shows some differences at more negative potentials related to the decomposition of the DES when water is present. CVs obtained in a DES system with 10 wt% water showed an additional reduction peak (D) close to the decomposition reaction when metal ions were present (Figure 11a and 11b). This reduction peak (D) is associated to a re-oxidation signal (D') when the hydrogen evolution reaction (B) is inhibited (Figure 11b), thus indicating that the reduction product is adsorbed on the substrate and can be removed by the hydrogen gas evolution. This peak was also observed in the work of Gamarra et al. (15), when the ChCl:EG ratio was changed from 1:2 to 1:4 in a solution with Fe(II) ions.

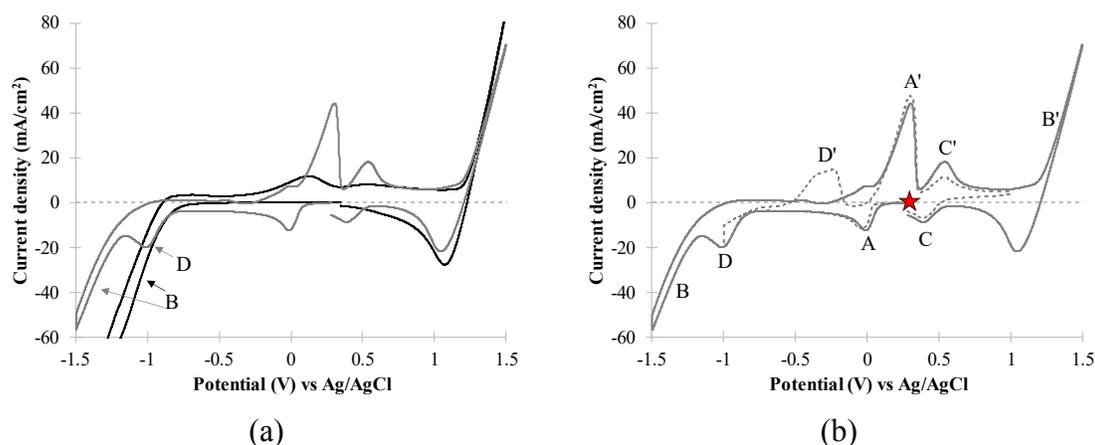


Figure 11. CVs obtained in 1ChCl:2EG with 10 wt% water, Pt substrate, scan rate 200 mV/s. (a) Pure DES (black line), and after addition of 100 mM Ag(I) and Fe(II) (grey line). (b) CVs obtained from the DES with 100 mM Ag(I) and Fe(II) added, at different vertex potentials.

Literature shows that the DES composition and substrate type have a significant effect on the electrochemical double layer, which again will affect the electrochemical reactions. Hammond et al. (21) showed the effect of water content on the interfacial arrangements of liquid components in DES, which was shown to be significant already by adding 10 wt% water.

In the study by Gamarra et al. (15) it was also observed that different composition of the DES strongly affected the electrochemical reactivity of iron, observing the same features in the cathodic reactions when changing the ChCl:EG ratio as in the present work with water additions. Gamarra et al. argued that the electrochemical processes related to DES decomposition was shown to be more complex when iron was present, making it difficult to determine if the observed differences was only caused by the change in electrochemical double layer, or if also the difference may be related to the speciation of Fe ions. Fe speciation has also been shown to be different based on the chloride:iron ratio by Miller et al. (14), affecting the Fe deposition mechanism, which, as explained above, occurs close to the cathodic decomposition of the DES electrolyte. The CV in Figure 11b does show a significant peak on the return scan when avoiding the dominating decomposition reaction, which may be a result of different adsorbed species and/or dissolution of deposited iron.

Despite the issues related to DES decomposition and possible enhanced Fe deposition in the presence of water, silver recovery with water present in the DES electrolyte is fully possible. This is confirmed by the SEM image in Figure 12, where a dense layer of Ag particles without any Fe detected was obtained despite 10 wt% water in the DES system.

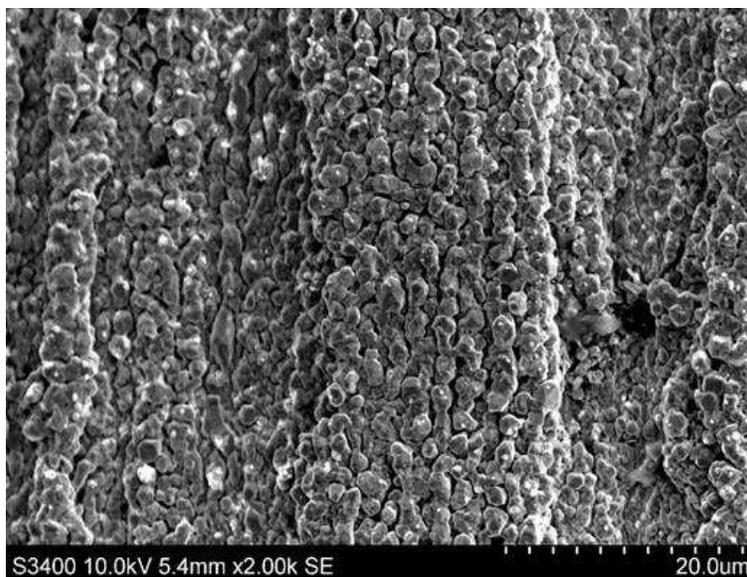


Figure 12. Ag deposit obtained on a Pt substrate at galvanostatic conditions ( $1.55 \text{ mA/cm}^2$ ) for 5 minutes under stirring of the DES solutions with 10 wt% water, 100 mM Ag(I) and Fe(II).

The average values of the EDS point analysis for deposits obtained on Pt in the different electrolytes throughout the paper is summarized in Table I, showing no significant differences between them. The detection of C, O, and small amounts of Cl is likely DES electrolyte remains, despite the substrate being rinsed in ethanol with an ultrasonic bath.

The results confirm that, given the same electrochemical species is present after leaching as when adding chlorides, the proposed recycling process could be used as a final step to recover metallic silver. As such, choosing suitable electrodeposition conditions to maintain controlled growth of Ag and avoiding Fe deposition and other side reactions is crucial, independently of water content.

**TABLE I.** Average EDS point analysis of silver deposits acquired on Pt from different DES electrolytes.

Electrolyte	Ag (wt%)	Fe (wt%)	C (wt%)	O (wt%)	Cl (wt%)
50 mM AgCl (9 points)	97.42	-	1.76	0.77	0.05
50 mM AgCl + 50 mM FeCl <sub>2</sub> (15 points)	97.17	0.00	2.07	0.56	0.21
50 mM AgCl + 50 mM FeCl <sub>3</sub> ·6H <sub>2</sub> O (7 points)	97.00	0.00	1.91	1.00	0.08
100 mM AgCl + 100 mM FeCl <sub>2</sub> + 10 wt% H <sub>2</sub> O (3 points)	97.86	0.00	1.61	0.49	0.05

## Conclusions

Electrochemical characterization of Ag(I) and Fe(II) ions in ethaline DES showed that the Ag(I)/Ag and Fe(III)/Fe(II) electrochemical systems were sufficiently far from each other to selectively recover Ag in the presence of Fe ions by electrowinning, as proposed in a recycling process for PV cells. The diffusion coefficients were determined from CV measurements, and found to be in the range of  $1.77\text{-}4.16 \cdot 10^{-7} \text{ cm}^2/\text{s}$  for Ag(I) and  $2.02\text{-}3.19 \cdot 10^{-7} \text{ cm}^2/\text{s}$  for Fe(II) ions. The differences in value obtained when using Pt or GC substrates could be due to the dissimilar electric double layer structure on the different substrates. High quality Ag deposits without presence of Fe ions were characterized on Pt, Ag and 316L stainless steel substrates, and the quality of the Ag deposit did not change by adding Fe(III) ions or up to 10 wt% water into the DES electrolyte. Adding water in the DES system gives the possibility of obtaining higher currents due to a less viscous solution, but it may result in an enhanced iron deposition reaction and/or decomposition of the DES electrolyte. The electrochemical results indicate that a process for recovering Ag from solar cell wastes using DES, FeCl<sub>3</sub> as oxidant, and subsequent electrowinning, should be possible, thus proposing a new, environmentally friendly solution to recover metallic Ag from production scrap and EoL solar cells.

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## References

1. V. Rai, D. Liu, D. Xia, Y. Jayaraman, and J.-C. P. Gabriel, *Recycling*, **6**(53) (2021).
2. E. L. Smith, A. P. Abbott, and K. S. Ryder, *Chem. Rev.*, **114**(21), 11060 (2014)

3. P. Dias, S. Javimczik, M. Benevit, H. Veit, and A. M. Bernardes, *Waste Manag.*, **57**, 220 (2016)
4. V. Agieienko and R. Buchner, *Phys. Chem. Chem. Phys.* **24**(9), 5265 (2022)
5. A. P. Abbott, K. E. Ttaib, G. Frisch, K. S. Ryder, and D. Weston, *Phys. Chem. Chem. Phys.* **14**(7), 2443 (2012)
6. N. G. Sousa, S. P. Sousa, O. S. Campos, P. de Lima-Neto, and A.N. Correia, *J. Mol. Liq.*, **288**, 111091(2019)
7. A. P. Abbott, G. Frisch, S. J. Gurman, A. R. Hillman, J. Hartley, F. Holyoak, and K. S. Ryder, *Chem. Commun.*, **47**(36), 10031 (2011)
8. Y. Chen, D. Yu, W. Chen, L. Fu, and T. Mu, *Phys. Chem. Chem. Phys.* **21**(5), 2601 (2019)
9. K. Haerens, E. Matthijs, K. Binnemans, and B. van der Bruggen, *Green Chem.*, **11**(9), 1357 (2009)
10. Y. Castrillejo, A. M. Martinez, R. Pardo, and G. M. Haarberg, *Electrochim. Acta*, **42**(12), 1869 (1997)
11. T. Berzins and P. Delahay, *J. Am. Chem. Soc.*, **77**(24), 6448 (1955)
12. R. Costa, A. T. S. C. Brandão, C. M. Pereira, A. F. Silva, *Electrochim. Acta*, **461**, 142653 (2023)
13. A. C. F. Ribeiro, L. M. P. Veríssimo, A. J. F. N. Sobral, V. M. M. Lobo, and M. A. Estesio, *C. R. Chim.*, **16**(5), 469 (2013)
14. M. A. Miller, J. S. Wainright, and R. F. Savinell, *JES*, **164**(4), A796 (2017)
15. J. D. Gamarra, K. Marcoen, A. Hubin, and T. Hauffman, *Electrochim. Acta*, **312**, 303 (2019)
16. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications* (2<sup>nd</sup> edition), Wiley, New York (2000)
17. J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948)
18. A. Ševčík, *Collect. Czech Chem. Commun.*, **13**, 349 (1948)
19. P. E. Valverde, T. A. Green, and S. Roy, *J. Appl. Electrochem.*, **50**(6), 699 (2020)
20. I. Alfurayj, C. C. Fraenza, Y. Zhang, R. Pandian, S. Spittle, B. Hansen, W. Dean, B. Gurkan, R. Savinell, S. Greenbaum, E. Maginn, J. Sangoro, and C. Burda, *J. Phys. Chem. B.*, **125**(31), 8888 (2021)
21. O. S. Hammond, H. Li, C. Westermann, A. Y. M. Al-Murshedi, F. Endres, A. P. Abbott, G. G. Warr, K. J. Edler, and R. Atkin, *Nanoscale Horiz.*, **4**, 158 (2019)