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Published in:
Journal of Cleaner Production

DOI:
[10.1016/j.jclepro.2024.144163](https://doi.org/10.1016/j.jclepro.2024.144163)

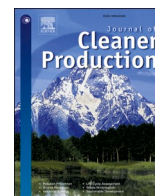
Published: 25/12/2024

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Cui, L., Herrala, R., Yliniemi, K., Vapaavuori, J., Sainio, J., & Lundström, M. (2024). Recovery of platinum from iron-containing chloride solutions through electrochemically assisted aqueous reduction. *Journal of Cleaner Production*, 485, Article 144163. <https://doi.org/10.1016/j.jclepro.2024.144163>

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Recovery of platinum from iron-containing chloride solutions through electrochemically assisted aqueous reduction

Linfan Cui^{a,b}, Reima Herrala^{a,b}, Kirsi Yliniemi^b, Jaana Vapaavuori^b, Jani Sainio^c, Mari Lundström^{b,*}

^a Department of Chemical and Metallurgical Engineering, Aalto University, Espoo, 02150, Finland

^b Department of Chemistry and Materials Science, Aalto University, Espoo, 02150, Finland

^c Department of Applied Physics, Aalto University, Espoo, 02150, Finland

ARTICLE INFO

Handling Editor: Yutao Wang

Keywords:

Metal recycling
electrochemical recovery
Hydrometallurgy
Low-grade raw materials
Precious metals

ABSTRACT

Precious metals are increasing in demand and consumption year by year, especially in the context of the renewable energy revolution. Depletion and scarcity of the world's natural resources calls for an attention shift to the recovery of secondary raw materials. Nevertheless, secondary resources, such as hydrometallurgical process solutions, also contain impurities. Herein, electrochemically assisted aqueous reduction (EAR) is studied to selectively extract platinum by utilizing multivalent dissolved iron species, which are typical impurities in hydrometallurgical solution. As a result, platinum with high purity was successfully recovered from the iron-containing chloride solutions, even when platinum was present at low concentrations. The reaction process of EAR was elucidated by the electro-gravimetric study. The deposition rate and morphology of platinum on the electrode can be flexibly controlled through operational parameters. The effect of the solution composition on EAR process was also investigated, providing potential industrial feasibility of EAR as a refining unit for valuable metals.

1. Introduction

The precious metals (PMs), consisting of a small portion in the Earth's crust, are critical components with high economic value in industry (Bildirci and Gokmenoglu, 2020). For instance, the platinum group metals (PGMs) are key catalysts for processing petroleum, purifying the gasoline exhaust, and converting CO₂ (Dong et al., 2018; Jiang et al., 2017; Trinh et al., 2020), etc. In addition, the development of automobiles that use renewable fuels, such as hydrogen, greatly increases the demand for PGMs in the future (Germescheidt et al., 2021; Ishaq et al., 2022). With extensive reliance on the primary metal production in recent years, their supplies are already insufficient, e.g., the demand for Pt during 2015–2020 is >250 tons/year, while the supply has been reported being <200 tons/year (Chen et al., 2021). The demand can be partially covered by the secondary resources, such as automobile catalytic converter materials (Rood et al., 2020), or the process solutions in the final stage of hydrometallurgical or

pyro-hydrometallurgical operations (Halli et al., 2018; Kalliomäki et al., 2019; Kangas et al., 2017; Maja and Spinelli, 1971). Indeed, various waste fractions that contain PMs have become crucial resources to contribute to the production of high-value goods and materials (Wang et al., 2017).

The PMs in secondary raw materials and side streams are generally recovered by metallurgical unit processes, e.g., via hydrometallurgical aqua regia dissolution extraction of solid Pt from e-waste or spent catalysts (Lin, 2012; Niemelä et al., 2012). After transferring from solid waste to liquid process solutions through hydrometallurgy, it is necessary to further extract and separate the dissolved PM ions either into reduced metallic form or into crystallized PM salts such as (NH₄)₂PtCl₆ (Barakat and Mahmoud, 2004; Liu et al., 2019; Maruyama et al., 2007). The electrochemical methods based on renewable energy without chemical additions have attracted considerable attention in PM recovery. Recently, the electrodeposition-redox replacement (EDRR) method has been employed to efficiently and selectively enrich and recover

Abbreviations: PMs, precious metals; PGMs, platinum group metals; EDRR, electrodeposition-redox replacement; EAR, electrochemically aqueous reduction; RE, reference electrode; CE, counter electrode; WE, working electrodes; EQCM, Electrochemical quartz crystal microbalance; SEM-EDS, Scanning electron microscope-energy dispersion spectroscopy; XPS, X-ray photoelectron spectroscopy; CV, cyclic voltammetry.

* Corresponding author.

E-mail address: mari.lundstrom@aalto.fi (M. Lundström).

<https://doi.org/10.1016/j.jclepro.2024.144163>

Received 30 January 2024; Received in revised form 22 September 2024; Accepted 3 November 2024

Available online 29 November 2024

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various PMs from industrial solutions, where PMs are present at low concentrations ($< \text{mg L}^{-1}$ or $< \mu\text{g L}^{-1}$) (Cui et al., 2023; Elomaa et al., 2018; Halli et al., 2017, 2018, 2020, 2021, ; Hannula et al., 2019b; Korolev et al., 2018, 2019, 2020; Molina et al., 2021; Wang et al., 2019). The recovered Pt by EDRR achieved ~ 90 wt% in the final deposition with a Pt/Ni enrichment ratio of 10^{11} from hydrometallurgical Ni process solutions (Ni: $> 140 \text{ g L}^{-1}$, Pt: $< 1 \mu\text{g L}^{-1}$) to recovered product (Halli et al., 2018).

In addition to the PMs, a variety of impurities are also present in industrial metallurgical solutions. Iron is one of the common impurities, originating from the components in the recyclable wastes (e.g., e-scrap), and minerals of the primary production (e.g., pyrite or chalcopyrite) (Korolev et al., 2019; Wang et al., 2019; Yliniemi et al., 2018). Platinum can be selectively extracted from the chloride leaching solution in the presence of the Fe by solvent extraction (Jha et al., 2014). In state-of-the-art industrial electrochemical recovery processes, such as electrowinning and newly developed EDRR, the Fe impurities are usually removed from hydrometallurgical processes before the target metal recovery (Izadi et al., 2017; Moskalyk and Alfantazi, 2002; Saba and Elsherief, 2000). The Fe impurities cause a decrease in the current efficiency of recovery due to the ferric to ferrous reduction at the cathode (Wang et al., 2019; Yliniemi et al., 2018). On the other hand, the presence of Fe may decrease the cell potential and thus provide advantage with less energy consuming anodic reaction compared to oxygen evolution (Hannula et al., 2019a). In previously reported EDRR technique, the ferric species exhibited a positive effect on the purity of the recovered PMs, such as recovered Ag by Zn in sulfate media (Wang et al., 2019) and Au by Cu in chloride media (Yliniemi et al., 2018), due to the spontaneous oxidation of sacrificial metals (Zn or Cu) by Fe(III). The zero-valent iron has also proven to efficiently enrich and recover Au and Ag from the wastewater through translocation (Ling et al., 2018).

Considering that Pt is usually present in hydrometallurgical solution along with Fe (Jha et al., 2014), in this work, the role of Fe on Pt recovery was investigated through an electrochemically aqueous reduction (EAR) process. In this recovery method, Fe(III) is first electrochemically reduced to its lower oxidation state, Fe(II), and the produced aqueous species are investigated as potential reductants to recover dissolved Pt without external applied potential. Fe(II) species have shown to have spontaneous redox reaction with Pt(II) in chloride based ionic liquids (Huang et al., 2010). In contrast to EDRR, the EAR method prevents the use of solid sacrificial metals as reductants, resulting high purity of the recovered metals. The utilization of aqueous reductant, Cu(I), has already been proved to recover Au in our earlier work (Herrala et al., 2023; Korolev et al., 2020). The roles of operational parameters and the compositions of the solutions on the Pt recovery were systematically studied, paving the way of the EAR to be applied for metal recycling from secondary resources.

2. Materials and methods

2.1. Chemicals

Chemicals used in this work include Pt AAS standard (1000 ppm of Pt (IV), Alfa Aesar, Germany), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.0\%$, Sigma-Aldrich, USA), NaCl (ACS reagent $\geq 99.0\%$, Sigma-Aldrich, USA), $\text{C}_6\text{H}_{12}\text{O}_6$ (VWR Chemicals, Belgium) and Phosphate buffer saline (PBS) (Tablet, Sigma-Aldrich, USA). All solutions are prepared with Millipore Milli-Q deionized water (DI water, $\geq 18 \text{ M}\Omega\text{-cm}$).

2.2. Equipment

The electrochemical measurements were conducted in a three-electrode cell system, with a 50 ml electrochemical cell, a saturated calomel as reference electrode (RE, B521, SI Analytics, SCE, $+0.241 \text{ V}$ vs. SHE), a counter electrode (CE) of platinum sheet, glassy carbon as working electrodes (WE) with a surface area of 1 cm^2 , and a potentiostat

(IviumStat 24-bit CompactStat (Ivium, NL). Electrochemical quartz crystal microbalance (EQCM, Biolin Scientific QSense) was used to study the relation between potential pulses and deposited mass with quartz QCM sensors (stainless steel coating) as WE, Ag/AgCl electrode as RE and Pt as CE, the flow rate of electrolyte was $200 \mu\text{L s}^{-1}$, series of data was measured at the same time when the system was stable with fresh quartz crystals. Scanning electron microscope-energy dispersion spectroscopy, SEM-EDS (Leo 1450 VP, Zeiss, Germany, INCA-software, Oxford Instruments, UK) was used for the morphology and chemical analysis of the deposits. The Pt/Fe ratios were calculated based on the average values of three EDS measurements for each sample (Table S1). X-ray diffraction (XRD) was conducted using PANalytical X'Pert PRO, samples were prepared with longer EAR cycles ($n = 500\text{--}1500$). X-ray photoelectron spectroscopy (XPS) was performed to study the chemical composition, using a Kratos Axis Ultra spectrometer with monochromated Al K α -radiation, an X-ray power of 150 W and an analysis area of approximately $700 \times 300 \mu\text{m}^2$. The pass energies/step sizes used were $40 \text{ eV}/100 \text{ meV}$ (high-resolution spectra) and $80 \text{ eV}/1000 \text{ meV}$. The binding energy scale was based on instrument calibration and no additional binding energy correction has been applied.

2.3. Experimental details

To reveal the characteristic oxidation and reduction behaviors of studied elements (Fe and Pt) as well as the effect of concentrations of Fe, Pt and Cl in the electrolytes on the oxidation and reduction reactions, the cyclic voltammetry (CV) measurements were conducted in electrolytes with different contents (Table 1). The CV was conducted starting from the measured open circuit potential of the WE into anodic direction up to 1.3 V vs. SCE and to the cathodic direction until -0.4 V vs. SCE was reached, then reversing again started towards open circuit potential. The scan rate was 50 mV s^{-1} . The last cycle was used to observe characteristic oxidation and reduction peaks of the voltammograms.

To electrochemically recover Pt by Fe, the designed process consists of two steps: 1) reduction of Fe(III) to Fe(II) at a pre-determined potential E_1 ($-0.4\text{--}0 \text{ V}$ vs. SCE), with a duration of t_1 ($3\text{--}10 \text{ s}$), and 2) the system is under open circuit situation for specific time t_2 to allow the spontaneous Pt reduction. The two steps are repeated for n cycles ($30\text{--}300$).

To interpret the mechanism in detail, electrogravimetry measurements by EQCM were combined with EAR experiments to define the reaction paths. EQCM data was analysed using the Sauerbrey equation (Eq. (1)):

$$\Delta m = -C \cdot \frac{\Delta f}{n} \quad (1)$$

where Δm is the change in mass, C is a crystal dependent constant, $C = 20 \text{ ng/Hz}$ for an AT-cut 5 MHz quartz crystal with an active surface area of 1.13 cm^2 , Δf is the frequency change, n is the resonance harmonic.

The current efficiency (η) and energy consumption (w) can be calculated as follows:

Table 1
Solutions for EAR measurements.

Solution No.	Pt (mg L^{-1})	Fe (g L^{-1})	NaCl (g L^{-1})	pH
1	50	–	5.8	1.2
2	–	5	5.8	1.9
3	50	5	5.8	1.1
4	50	10	5.8	1.1
5	50	1	5.8	1.2
6	50	5	29	1.1
7	50	5	58	0.9
8	30	5	5.8	1.2
9	10	5	5.8	1.6

$$\eta = \frac{\Delta m \cdot \nu \cdot F}{Q \cdot M} \quad (2)$$

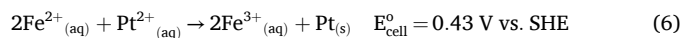
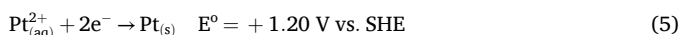
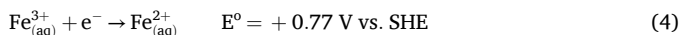
$$w = \frac{Q \cdot E_{\text{cell}}}{3600 \cdot m} \quad (3)$$

where ν is the number of electrons transferred in the reaction, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), Q is the total measured charge, M is the molar mass, m is mass of Pt.

3. Results and discussion

3.1. EAR process to recover Pt assisted by Fe

To electrochemically extract dissolved Pt with Fe through the EAR method (Fig. 1a), dissolved Fe(III) in chloride-based media is first reduced to a lower oxidation state Fe(II) with a potential E_1 for a defined duration t_1 (Eq. (4)). The deposition of Pt may also occur simultaneously during this step (Eq. (5)). In the second step, the system is left in open circuit conditions with a predetermined t_2 , and the produced aqueous Fe(II) species serves as a reductant to reduce the dissolved Pt in the solution (Eq. (6)). The two consecutive steps are continuously repeated after each other.



To determine the applied potential E_1 , the electrode potentials for redox reactions of Fe(III)/Fe(II) were experimentally studied through CV (Fig. 1b). In Pt-Fe-Cl contained electrolyte (solution 3), the cathodic reduction peak (p_{c1}) for Fe(III)/Fe(II) was observed at ca. 0.4 V vs. SCE, which was identified at 0.2 V vs. SCE in the Fe-Cl contained solution (Solution 2). The Fe-Cl complexes, such as FeCl^{2+} (Figs. S1 and S2) formed in the electrolyte are known to impact the reduction potentials of Fe(III)/Fe(II), resulting in shifted values that differ from their standard redox potential (E° in Eq. (4)) (Heinrich and Seward, 1990; Tagirov et al., 2000). Two anodic peaks around potentials of 0.4 V (p_{a1}) and 0.9 V (p_{a2}) vs. SCE were observed in Fe-Cl contained electrolyte (solution 2), which were also detected in Pt-Fe-Cl contained electrolyte (solution 3) with potential shifts. The reduction of Fe(II) to Fe(0) may partly (Eq. (7)) occur when conducting CV in the cathodic direction negative to -0.4 V vs. SCE (Fig. 1b). Therefore, the anodic peak (p_{a2}) for the re-oxidation of the formed Fe(0) (at p_{c1}) was overlapped with the oxidation peak (p_{a1}) for Fe(0) to Fe(II). Similar phenomenon was also found in other Pt-Fe-Cl contained system (Huang et al., 2010). When measuring CV in the cathodic direction until -0.2 V vs. SCE in solution 3 (Fig. S3), only a single pair of redox peaks corresponding to Fe(III)/Fe(II) were detected, and the reduction of Fe(II) to Fe(0) did not occur. In Pt-Fe-Cl contained electrolyte (solution 3), no obvious Pt reduction peak was observed (Fig. 1b), nevertheless, a Pt reduction peak of Pt was shown at approximately 1.0 V vs. SCE in the Pt-Cl contained electrolyte without Fe

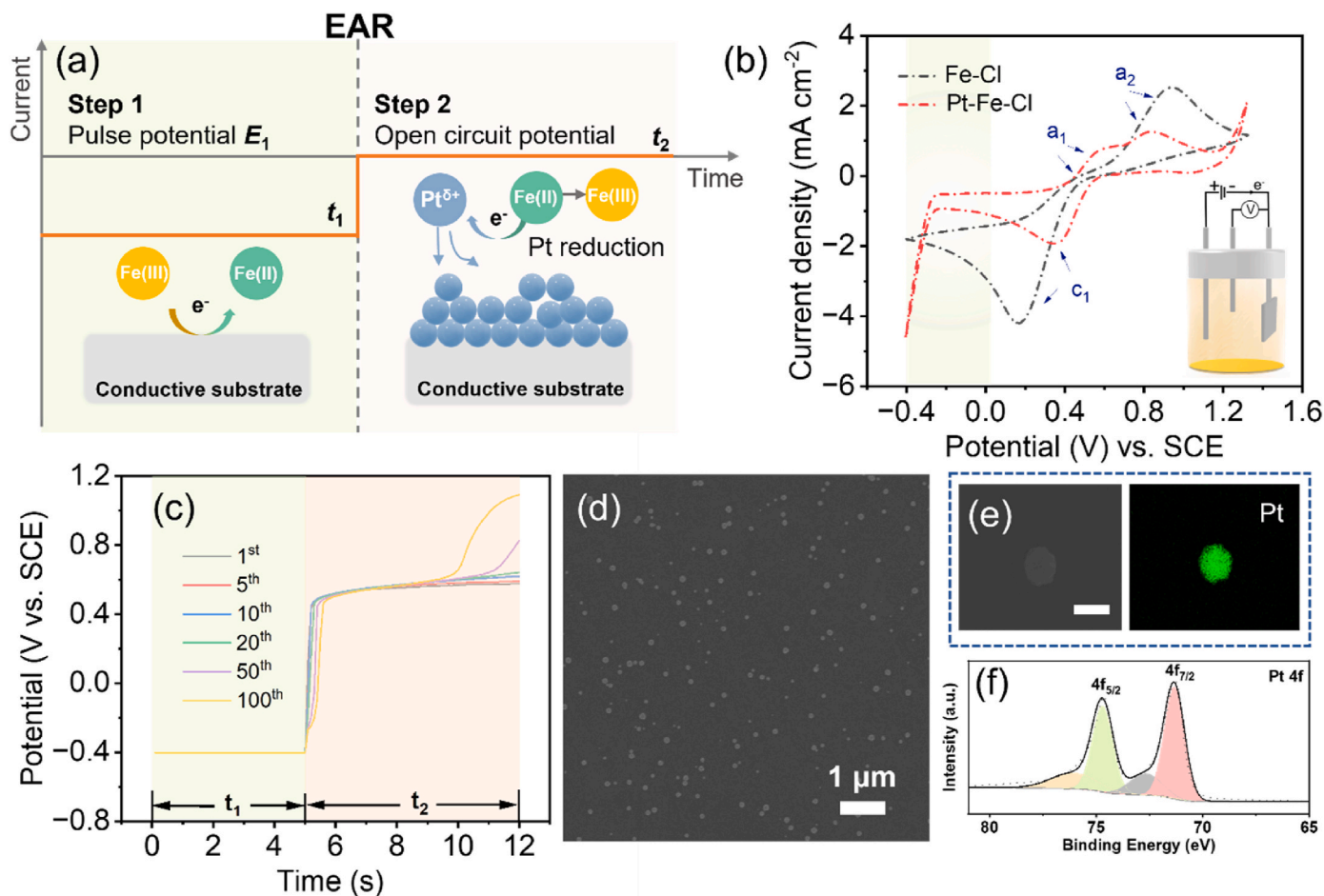
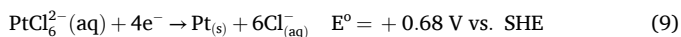
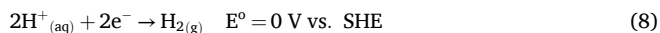
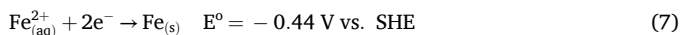


Fig. 1. EAR process for the recovery of Pt. (a) Schematic of the EAR process. (b) CV plots using glassy carbon WE measured in the Fe-Cl (solution 2) and Pt-Fe-Cl contained (solution 3) electrolytes (solution 3). (c) Typical potential-time plots for the EAR protocol in Pt-Fe-Cl-contained electrolyte. (d) SEM, (e) EDS mapping images (scale bar: 100 nm) and (f) high resolution XPS Pt 4f spectrum of the deposits prepared by EAR methods (c–f: $E_1 = -0.4 \text{ V vs. SCE}$, $t_1 = 5 \text{ s}$, $t_2 = 7 \text{ s}$, $n = 100$, in solution 3).

(Fig. S4). It is worth noting H_2 evolution occurred (Eq. (8)) in the Pt containing solution (solution 1 and 3) at cathodic potential of -0.3 V vs. SCE in Fig. 1b and S3a. In comparison, the H_2 was not formed even at the cathodic potential of -0.44 V vs. SCE in the electrolyte without Pt (solution 2). The catalytic effect of Pt was evident in facilitating H_2 formation, proving the initiation of Pt reduction on the electrode surface during the CV measurement in solution 3. Platinum also forms chloride complexes (e.g., $PtCl_4$, Fig. S1), affecting the redox behavior (Eq. (9)) (Kravtsov, 2000; Sun et al., 2022) and making Pt to become less noble.



The potential E_1 was chosen to be more cathodic relative to the reduction potential of $Fe(III)/Fe(II)$ to support the presence of reductive $Fe(II)$ in the solution. However, the applied E_1 was also considered to minimise the H_2 evolution and related energy consumption. The t_2 in the second step should allow sufficient time for the reduction of Pt. A typical profile of the EAR process is shown in Fig. 1c with an initial applied potential E_1 at -0.4 V vs. SCE for $t_1 = 5$ s, followed by the step with open-circuit potential for $t_2 = 7$ s, and the entire process consists of 100 cycles of EAR. Considering the continuous Pt deposits formed on the electrode with extended duration of t_2 , the potential of the electrode also increased during the second step of EAR process (Fig. 1c). As a result, high purity Pt particles (95.0 wt%) were uniformly deposited onto the glassy carbon electrode surface (Fig. 1d and e), the results were matched with XRD pattern for Pt product (Fig. S5).

According to Pt 4f XPS spectrum (Fig. 1f), two main peaks centered at around 74.7 eV and 71.3 eV were ascribed to Pt^0 4f_{5/2} and Pt^0 4f_{7/2}, belonging to the metallic Pt in the deposits. And the Pt^{2+} 4f_{7/2} with binding energy at around 72.7 eV indicated the Pt-O bond from the oxidized Pt (Asami et al., 2019; Lu et al., 2016). The Fe 2p_{1/2} and Fe 2p_{3/2} peaks were also detected, corresponding to presence of metallic

Fe, $FeCl_3$ and/or Fe_2O_3 (Fig. S6) (Xu et al., 2020; Yamashita and Hayes, 2008). This was consistent with the CV results (Fig. 1b), lower Fe content was also detected through EDS (Fig. 1e).

3.2. Electrogravimetric study of the EAR process

To track the Pt deposition during the EAR process, the faradaic and gravimetric study were conducted simultaneously by EQCM. During the total 30 cycles of EAR process (Fig. 2a), an increasing trend in mass was observed. In one cycle of EAR, as shown in Fig. 2b, the deposition was detected in both steps. The mass increase at the end of the first EAR step indicated the occurrence of deposition (light green area in Fig. 2b). To confirm the deposition obtained with the applied E_1 during EAR, the mass variation on the electrode by only applying constant potential ($E = -0.4$ V vs. SCE) were measured in both Fe-Cl and Pt-Cl contained solutions. As shown in Fig. 2c, the deposition in Fe-Cl contained solution was inconspicuous, while the mass change in Pt-Cl contained solutions was clearly observed, indicating the main content in formed deposits during the first EAR step was Pt. Moreover, upon constant potential deposition applied in the Pt-Fe-Cl solution, the contents of Pt in the deposited particles were 96.2 ($E = -0.4$ V), 97.1 ($E = -0.3$ V), 100.0 ($E = -0.2$ V) and 100.0 wt % ($E = -0.1$ V) (Fig. S7). This further confirms that the mass change in the first step of EAR process mainly originates from the formation of Pt.

When the potential is switched off and cell is under open circuit potential, the reduction of Pt by aqueous $Fe(II)$ occurs. The mass-change in this step started with a sharp growth within the first few seconds and tended to saturate during the rest of the step (light red region in Fig. 2b). The quick mass buildup is related to Pt accumulation via the reactions with aqueous $Fe(II)$ species. When the $Fe(II)$ is consumed and limited in the vicinity of the cathode, less amount of Pt are produced on the electrode, leading to moderate mass variation and dropped deposition rate. Moreover, the H^+ ions are relatively abundant around the electrode. Competing oxidation of $Fe(II)$ by H^+ may also happen, and the reductant $Fe(II)$ is thus consumed. A similar phenomenon was also

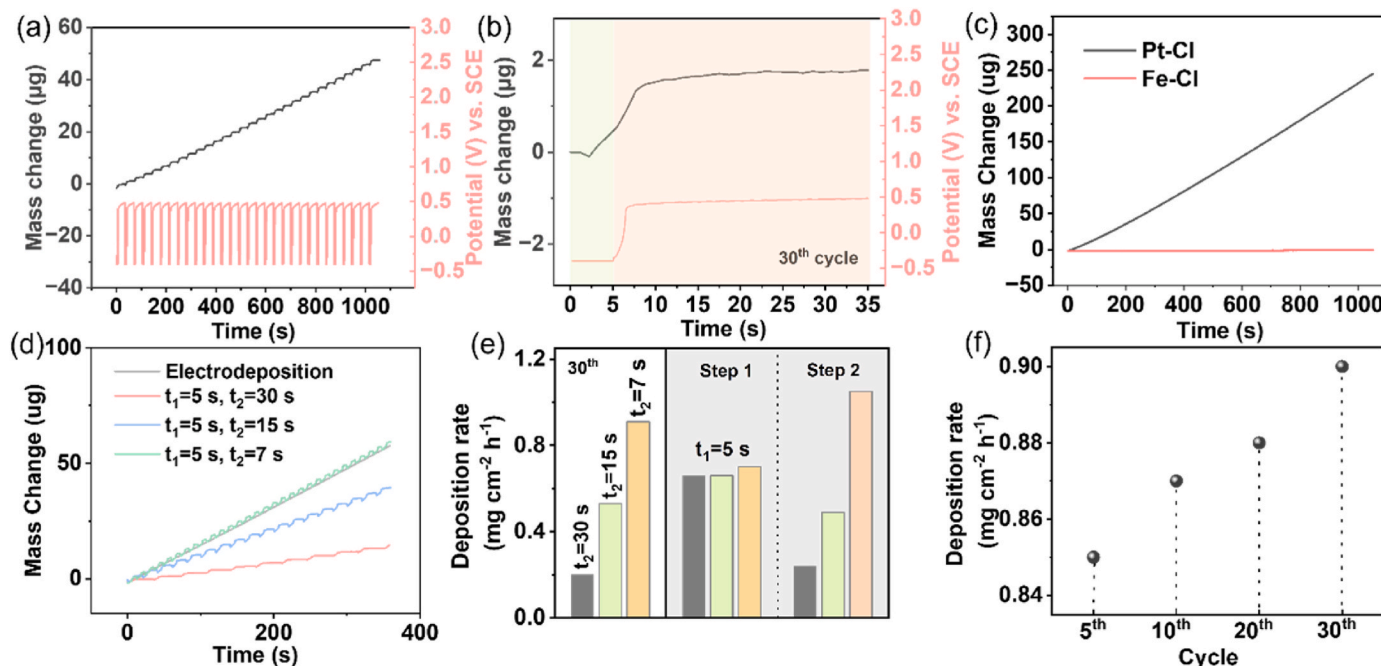


Fig. 2. Measured potentials and mass change during the EAR process ($T = 25$ °C). (a) Mass and potential change throughout 30 EAR cycles and (b) variation for one EAR cycle ($E_1 = -0.4$ V vs. SCE, $t_1 = 5$ s, $t_2 = 30$ s in solution 3). (c) Mass change when applying constant potential of -0.4 V vs. SCE on the glassy carbon electrode in the Pt-Cl (Solution 1) and Fe-Cl (Solution 2) contained electrolytes. (d) The influence of t_2 on the mass variation during EAR process and mass change during the electrodeposition only applying with constant potential ($E = -0.4$ V vs. SCE) in the electrolyte (Solution 3). (e) Calculated deposition rates for EAR processes with various t_2 ($E_1 = -0.4$ V vs. SCE, $t_1 = 5$ s, in solution 3). (f) Calculated deposition rate of different EAR cycles ($E_1 = -0.4$ V vs. SCE, $t_1 = 5$ s, $t_2 = 7$ s, in solution 3).

observed in EDRR during the Ag recovery process by Zn, where Zn was partly consumed by H^+ (Wang et al., 2021). Thus, the deposition rates of the EAR process can be controlled through adjusting t_2 , shorter the t_2 , higher the deposition rate was achieved (Fig. 2d and e). In comparison, when applying constant potential under same value with E_1 , the electrodeposition rate for Pt was faster than most of the EAR processes (Fig. 2d). Generally, longer application of potential favors the formation and crystallization with a greater quantity of nuclei for further growth of the deposited metals (Duarte et al., 2006). When the t_2 was 7 s, the mass change of EAR process for Pt deposition was comparable with electrodeposition conducted with constant potential (Fig. 2d). Moreover, the mass increase during the 2nd step is higher ($t_2 = 7$ s), indicating more Pt can be recovered without external applied potential during EAR process (Fig. 2e). It was also shown that the deposition rate of each EAR cycle increased when extending the EAR cycles (Fig. 2f), while the cathodic current density also increased (Fig. S8). It is speculated that the Pt nuclei formed at initial EAR cycles facilitate the growth of Pt around these nuclei in the subsequent cycles; therefore, lower overpotential could be used after the nucleation formed during the initial cycles (Duarte et al., 2006). Similar phenomenon was also observed during EDRR process, where the Cu-Au layer formed at early stage efficiently dropped the potential for the following electrocrystallization of sacrificial Cu and then promoted the recovery amount of target Au on the cathode (Korolev et al., 2022).

3.3. Influence of the EAR parameters on Pt recovery

As discussed above, the deposition rate of EAR process can be controlled with t_2 . Other operational parameters during EAR, for instance, various E_1 (-0.4 – 0 V vs. SCE) and t_1 (3–10 s) were also applied to investigate their influence on the Pt reduction (Table S1).

It was shown that larger overpotential in the first step resulted in higher amount of Pt reduction (Fig. 3a), the deposition mass when $E_1 = -0.4$ V vs. SCE was around 2.5 times than that when $E_1 = -0.2$ V vs. SCE. The current densities (in 30th EAR cycle) were -7.2 mA cm^{-2} ($E_1 = -0.4$ V vs. SCE), -4.7 mA cm^{-2} ($E_1 = -0.3$ V vs. SCE), -4.4 mA cm^{-2} ($E_1 = -0.2$ V vs. SCE), -3.8 mA cm^{-2} ($E_1 = -0.1$ V vs. SCE), and the higher current density of $E_1 = -0.4$ V vs. SCE proves more efficient reduction. According to the EQCM measurement (30th cycle), the deposition rates of the first step were 0.70 mg $cm^{-2} h^{-1}$ ($E_1 = -0.4$ V vs. SCE), and 0.39 mg $cm^{-2} h^{-1}$ ($E_1 = -0.2$ V vs. SCE). Larger overpotential favors the formation and crystallization of Pt nuclei (Choi et al., 1998). Different E_1 also showed influence on the deposition rates during the second step of EAR (30th cycle), of which were 1.05 mg $cm^{-2} h^{-1}$ ($E_1 = -0.4$ V vs. SCE) and 0.32 mg $cm^{-2} h^{-1}$ ($E_1 = -0.2$ V vs. SCE). More negative E_1 promotes the accumulation of reductive Fe(II) around the cathode for the reduction of dissolved Pt during the second step of EAR. The evolved H_2 (when $E_1 < 0.3$ V vs. SCE, according to CV in Fig. 1b) was also assumed to facilitate the Pt reduction and contribute to the positive mass change (Wang et al., 2021). However, the formation of H_2 consumed part of the electric charge, affecting current efficiency for end-of-product. Although more deposition was obtained when $E_1 = -0.4$ V, the current efficiency was 19 %, which was close to that for E_1 set to -0.3 V (20 %). The reason for such a low efficiency is H_2 evolution, as CV measurements (Fig. 2b) showed that hydrogen evolution already commences at -0.4 V, and the energy consumption per mass of Pt is 1.25 kWh kg^{-1} . When $E_1 = 0$ V vs. SCE, no deposition was observed on the electrode surface (Fig. S9). With lower overpotential applied, the movement rate of electrons at the electrode surface may be insufficient for the Pt nuclei to be formed, thus resulting scarce sites for the Pt deposition (Choi et al., 1998).

The amount of deposited Pt also varied with t_1 (Fig. 3d, $E_1 = -0.2$ V vs. SCE), the lowest mass increase was obtained on the electrode when $t_1 = 3$ s. However, this tendency was not indefinite, the deposition rate for $t_1 = 10$ s was lower compared to $t_1 = 5$ s. To further study the influence of t_1 on the EAR process, the deposition rates of the two steps of

EAR (30th cycle) were compared. During EAR step 1, the deposition rates were 0.07 mg $cm^{-2} h^{-1}$ ($t_1 = 3$ s), 0.39 mg $cm^{-2} h^{-1}$ ($t_1 = 5$ s), 0.15 mg $cm^{-2} h^{-1}$ ($t_1 = 10$ s). Maintaining the same value for t_2 , the deposition rates of the second step were 0.27 mg $cm^{-2} h^{-1}$ ($t_1 = 3$ s), 0.32 mg $cm^{-2} h^{-1}$ ($t_1 = 5$ s), and 0.23 mg $cm^{-2} h^{-1}$ ($t_1 = 10$ s). Longer t_1 caused more Pt nuclei formed and growth. When increasing t_1 to 10 s, the competing reactions of H_2 evolution, oxidation of deposited Pt or Fe(II) oxidized by H^+ may occur and become more obvious (Wang et al., 2021), reducing the amount of reductive Fe(II) and the Pt nuclei and/or deposits formed during the first step. As a result, the corresponding recovered amount of Pt during step 2 exhibited no increase.

The Pt recovered under various E_1 and t_1 conditions exhibited high purity (>95.0 wt%). Small portions of Fe were detected in the deposits when a higher overpotential E_1 was applied (EDS results in Fig. 3 and S10). Additionally, larger Pt deposits were also obtained with more negative E_1 or longer t_1 (SEM in Fig. 3 and S10, Table S1). The application of a higher overpotential pulse promotes the formation of a greater quantity of nuclei and allows further deposition along the same sites, resulting in an increase in the size of the deposits when extending the t_1 (Rao and Trivedi, 2005). It should be noted that, when $E_1 = -0.4$ V vs. SCE, the particles were smaller (Figs. 1d and 87 ± 26 nm), albeit with larger deposition amount (Fig. 3a). Although the formation rate of Pt nuclei increased with more overpotential, metal ions to be deposited around cathode are exhausted gradually, causing scarce growth of the Pt deposits and leading to smaller particle size (Cheh, 1971; Choi et al., 1998; Ibl, 1980). The H_2 adsorption also introduces inaccuracies in determination of the electric charge used in the Pt electro-reduction and affect the formation process of the deposits (Mikhaylova et al., 2000). When the solution was stirred during EAR process ($E_1 = -0.4$ V vs. SCE), the size of the deposits (130 ± 30 nm) increased slightly (Fig. S11), due to the enhanced mass transfer. The EAR method with amendable operating parameters showed flexibility to control the deposition amount and particle size, suggesting its potential to adjust and optimize the recovery process of the target metal productions.

3.4. Influence of the electrolyte composition on Pt recovery

The Fe and Cl concentrations were shown to have a substantial impact on the Pt recovery, both on recovery amount and size of deposits (Fig. 4a–f). Among all the studied electrolytes (Table 1), the pH was ranging from 0.9 to 1.9, when increasing the pH to 2.5, aggregation was observed (Fig. S12), indicating the preferred pH range for EAR method. The influence of Fe and Cl concentrations is suggested to be associated with the complexation of Fe in chloride-based media (Figs. S1 and S2). As shown in Fig. 4a and d, the reduction potential for Fe(III)/Fe(II) shifted to negative direction with an increased concentration of Fe and Cl, possibly due to the strong ligand effect of Cl. As a result, more overpotential is required to reduce Fe(III), and fewer and smaller Pt particles were observed (Fig. 4b,c,e,f). When increasing the Fe concentration, the overlapping anodic peaks become stronger with higher oxidation current density (Fig. 4a): only one oxidation peak was detected in the anodic direction when $Fe = 1$ g L^{-1} while at 10 g L^{-1} there were overlapping oxidation peaks. The overlapping anodic peaks also altered with the concentration of Cl (Fig. 4d). With lower Fe (e.g., 1 g L^{-1}) and high Cl concentration (e.g., 58 g L^{-1}) in the studied chloride solutions, the reduction of Fe(II) to Fe(0) seems to disappear, and the purities of Pt deposits recovered from those two solutions were nearly 100 wt%.

The effect of Pt concentration in the electrolytes was also studied (Fig. 4g–i). As shown in Fig. 4h and i, the Pt particles can be deposited on the electrode surface at the concentration of Pt as low as 10 mg L^{-1} . The particle size and deposition amount decreased with lower Pt concentration, which was related to mass transfer limitations and corresponding slower deposition rate. Furthermore, the reduction potential for Fe(III)/Fe(II) was also observed with a shift to negative direction in lower Pt concentration solution (Fig. 4g), leading to an increased

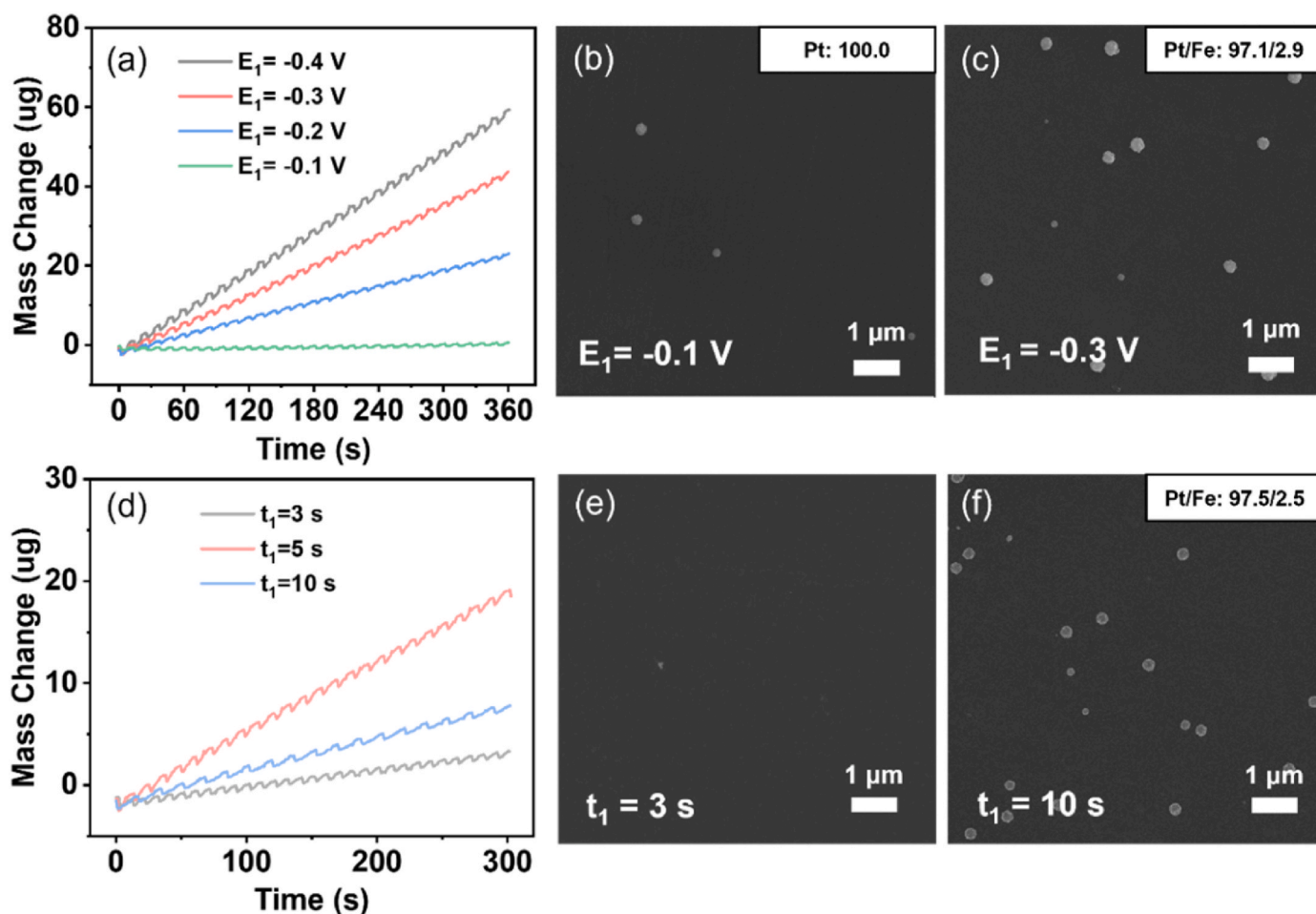


Fig. 3. Mass-change and SEM images of Pt recovered by EAR method with different operational parameters. (a–c) Different E_1 ($t_1 = 5$ s, $t_2 = 7$ s, $n = 100$ in b and c). (d–f) Different t_1 ($E_1 = -0.2$ V, $t_2 = 7$ s, $n = 100$ in e and f). Electrolyte: 50 mg L⁻¹ Pt, 5 g L⁻¹ Fe and 5.8 g L⁻¹ NaCl (Solution 3).

overpotential required to drive the reactions. However, bigger and more Pt particles can be still obtained at lower Pt concentration through extending the EAR cycles and stirring the solution, dendritic morphologies were also observed (Fig. S13). Overall, the results demonstrated the feasibility of recovering Pt by EAR method even at dilute Pt solutions with the presence of Fe, also suggesting the feasible operating range of EAR in real industrial process solution.

4. Conclusion

This work comprehensively investigated the EAR process for Pt recovery with assistance of typical impurity iron in the hydrometallurgical process solution. EAR process consists of two consecutive steps which can be repeated in cycles. Aqueous Fe(II) is first electrochemically produced with an applied potential, which was determined from the CV studies in the electrolyte. Metallic Pt is also partially electrodeposited during the first EAR step. External potential is then cut off to leave the system in an open circuit potential, where the produced Fe(II) species serve as reductant for the further reduction of dissolved Pt in the electrolyte. As a result, Pt was shown to be successfully recovered with a high purity of approximately 100 wt% on the electrodes by the EAR method. A substantial portion of the Pt can be obtained during the EAR process without the external applied potential.

The operating parameters of EAR and composition of the electrolyte affected the deposition process, including the deposition amount and the size of the Pt deposits. Applying larger overpotential (E_1) during the first step promoted the deposition of Pt, however, current efficiency was limited due to the competing H₂ evolution. By tailoring the t_1 and t_2 , the

deposition rates of EAR can be controlled and were deemed comparable to the electrodeposition process applied with constant potential during the whole process. The Pt-Cl and Fe-Cl complexes formed in the chloride solution also showed a substantial effect on the recovery of Pt, higher concentration of Fe and Cl resulted in less Pt formation and smaller particle size. The EAR method can efficiently achieve the recovery of the Pt at the concentration as low as 10 ppm. Extending the EAR cycles or agitating the solution also promoted the recovery process.

Overall, EAR method shows promise for efficiently recovering Pt at low concentration by utilizing the common impurity present in industrial process solutions. The process also exhibits potentials in integrating into hydrometallurgical process flows as a refining unit and contributing to the conservation of valuable resources. In our future work, EAR will be extended to complex industrial solutions containing more compounds and impurities to study their influence on efficiency and dynamics of Pt recovery. Furthermore, the study seeks to explore the compatibility of EAR on various substrates with controllable metal support, aiming to convert lower-grade resources into functional materials and enhancing the overall efficiency of the process.

CRediT authorship contribution statement

Linfan Cui: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Reima Herrala:** Writing – review & editing, Methodology, Investigation. **Kirsi Yliniemi:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Jaana Vapaavuori:** Writing – review & editing, Supervision, Resources, Funding acquisition,

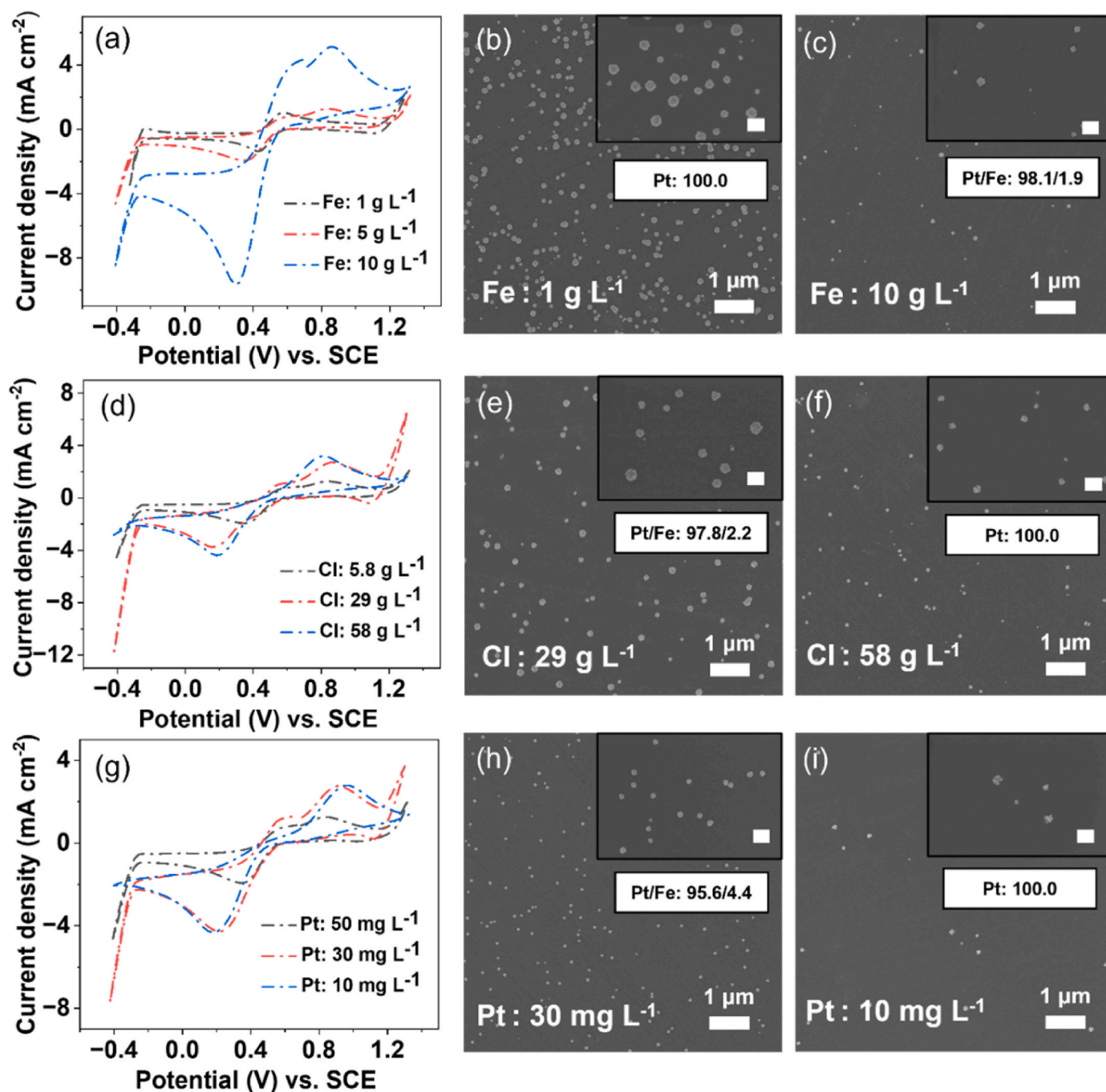


Fig. 4. Influence of electrolytes on the EAR process. (a, d, g) CV (scan rate: 50 mV s⁻¹) in solutions 3–9. (b, c, e, f, h, i) SEM images of the deposits on the glassy carbon electrode after EAR in solutions 4–9. Scale bar in insert images, 200 nm. (a–c) Solution 3, 4 and 5 with different Fe concentration. (d–f) Solution 3, 6 and 7 with different Cl concentration. (g–i) Solution 3, 8 and 9 with different Pt concentration. EAR parameters: $E_1 = -0.4$ V vs. SCE, $t_1 = 5$ s, $t_2 = 7$ s, $n = 100$.

Conceptualization. Jani Sainio: Writing – review & editing, Formal analysis, Data curation. Mari Lundström: Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Research Council of Finland project EARMetal (LC, KY, ML: 339979 and LC, KY, JV: 342080). The Raw-MatTERS Finland Infrastructure (RAMI) funded by the Research Council of Finland and based at Aalto University is acknowledged. We acknowledge the provision of facilities and technical support by Aalto University at OtaNano – Nanomicroscopy.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2024.144163>.

[org/10.1016/j.jclepro.2024.144163](https://doi.org/10.1016/j.jclepro.2024.144163).

Data availability

Datasets are available at Zenodo 10.5281/zenodo.10581798

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