Elucidating the Influence of Electrolyte Additives on Iron Electroplating Performance

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Abstract:
Iron electroplating is a process of great interest for many large-scale industrial and emerging energy applications, such as all-iron redox flow batteries. However, the process efficiency and material lifetime are greatly conditioned and limited by the poorly understood plating process and the presence of competitive reactions. In this work, we propose a methodology to deconvolute the nucleation parameters of iron via a suite of electrochemical techniques, spectroscopy, and analytical models, coupled with microscopic and crystallographic techniques. We perform a systematic analysis with iron-based electrolytes to deconvolute the simultaneous plating and hydrogen evolution reactions, and investigate an array of additives to tune electroplating descriptors. We find that all additives studied are able to regulate the plating process and find that highly stable iron-complexes based on buffers, such as iron-borates or -citrates deliver greater overall electroplating performance. These additives show superior selectivity, with improvements in faradaic efficiencies from 60% to ~90% due to the balanced effects of enhanced nucleation and side reaction suppression. Herewith, the aim of this study is to bridge the knowledge gap between the role of additives, kinetics and efficiency of the electrodeposition reaction, and their interplay defining the quality of the resulting plated layers.

Keywords: iron electroplating, electrolyte engineering, electrochemical engineering, all-iron redox flow batteries
1. INTRODUCTION

Electrochemical technologies are powerful candidates to aid in the transition to a more sustainable and decentralized renewables-based energy economy. In this new paradigm, large-scale energy storage will play a central role in the integration of renewable energy technologies[1–3]. Among the available options, redox flow batteries (RFBs) offer a strong alternative to overcome the primary challenges of these renewable sources, such as geographical constraints or mismatch for demand and supply at the grid level[4,5]. The principle behind RFB operation allows to meet many of the prerequisites needed for large-scale grid storage, such as a rapid response to variations in energy loads or inputs, high round-trip efficiency and high calendar life or sustained cyclability[6]. RFBs possess the ability to separate power and energy sizing or rating - the chemical energy is stored in the electrolyte solution containing the charge-carrying active species, stored in external tanks. The electrolyte solutions are pumped through the electrochemical stack, which determines the power of the system[7]. The stack is oftentimes the most expensive component, and is comprised mainly of bipolar plates, electrodes and membranes or separators[8]. The ability of RFB systems to independently scale-up power and energy offers potential for economic scaling[9].

Widespread deployment of RFBs is however currently restricted by elevated costs and materials availability[10,11]. Aqueous all iron-based flow batteries (AIBs) offer great potential as a low-cost and high-power energy storage and conversion system[12] due to their operation based on earth-abundant and environmentally benign materials and green solvents, such as water. Additional benefits of this type of redox flow batteries comprise large theoretical volumetric capacity and specific energy density (170 W h kg$_{\text{iron}}^{-1}$ in all iron configuration)[13–15], non-toxicity and non-flammability[16]. However, the capacity of AIBs, power output and cyclability are greatly influenced by the irregular plating and stripping process in the negative half-cell, and the presence of side reactions, such as gas evolution[17,18]. These phenomena generate irregular morphologies or defects and pitting seeds, resulting in an irregular current density distribution, which is further aggravated by operation at high current density or high specific capacities[19,20]. In the most extreme cases, this could lead to formation of dendritic structures, which has been proven to exacerbate uneven current distribution profiles, and induce non-homogeneous flow distribution, mass transport limitations[21–23], battery short-circuit, and...
sudden battery death[14]. Nevertheless, most studies focus on the plating process pertaining to the more common lithium- or zinc-based battery technologies[24–28]. However, the specific mechanisms of the plating and dissolution process of the anode, as well as their effects on the battery lifetime and performance, of the emerging all-iron aqueous system still remains poorly understood.

Achievement of uniform, defect free, abundant and well distributed nucleation and epitaxial growth and dissolution could ensure reversible operation, and the ability to sustain extended cycling performance. Common strategies to fine-tune the plating and stripping process and hydrogen evolution reaction (HER)-related inefficiencies, are based in the generation of coatings on the electrode[29,30] or electrolyte engineering[17,31,32]. The HER kinetics are strongly pH-dependent, and they can be inhibited by neutral or even slightly alkaline pH levels. However, this has an undesirable effect on the stability of iron species, particularly the Fe$^{2+}$ ion, as pH > 3 causes precipitates in the form of oxides or hydroxides with the subsequent loss in capacity, limiting the use of pH as a practical tool for AIB regulation. Consequently, the use of additives is one of the main tools employed to optimize AIB performance. Hawthorne et al. investigated the effects of several organic ligands, such as citrates, dymethil sulfoxide, glycine, malic acid or xylitol, among others, on the solubility, diffusion rate and redox kinetics towards all iron battery operation. They found that glycine was one of the most promising additives in the range of 0.5:1 to 1:1 (glycine : total iron), allowing for increases in pH that would reduce HER-induced losses by a factor of ~4, and without significant precipitation of iron. However, they also observed that additives in the electrolyte could also negatively affect the plating kinetics, shifting the onset value for deposition towards more negative potentials. Therefore, the selection of additives for iron-based batteries has to be carefully screened to optimize performance[17,33]. Additionally, Noack et al. further investigated the effect of electrolyte pH, temperature and composition, with a focus on the use of metal cations. They found that increases in operating temperature favor both hydrogen- and iron-reduction reactions, although the latter was preferentially enhanced, thus resulting in increased coulombic efficiencies up to 80 °C. They also demonstrated the advantages of fine tuning the electrolyte composition, reporting that the addition of low concentrations of metals such as Na$^+$ or Li$^+$ could substantially decrease iron plating overpotential without significantly altering the rate for hydrogen evolution, although the underlying mechanisms remain to be elucidated[32]. Furthermore, Eaves-Rather et al.
investigated the effect of kinetic and diffusion regimes for electroplating of bivalent metals with a focus on magnesium-based batteries. They observed the occurrence of preferential deposition exacerbating unevenness in the structure of the plated layer, greatly influenced by the transport properties of the electrolyte components. They employed Mg^{2+}|Mg symmetric cells and highlighted the dependence of magnesium nucleation and growth on the applied current, concentration of cations near the electrode surface, or increasing inter-electrode separation, with special attention on the resulting geometry, and found that current density and ion concentration strongly condition the interaction among the depositing metallic atoms. Thus, this favored the formation of thin, planar layers as opposed to tridimensional structures in the form of randomly located and oriented dendrites. This is critical towards battery performance, as the latter exacerbate mass transport challenges, current fluctuations and cell shorting[34]. Nevertheless, the intrinsic mechanism of electroplating for all-iron batteries, and its interplay with the characteristics of the electrodeposited layer and the cyclability of the system has not yet been researched, which represents a major limitation towards achieving high power metal plating batteries[35]. While this study focuses primarily on iron-based flow batteries, it introduces an approach extensible to other RFB chemistries and the many industrial systems that rely on plating and stripping of metals: due to its abundance and desirable physicochemical properties, iron is used on the largest scale of any metal and has numerous technical and scientific applications[36]: the process of obtention, refinement, processing and disposal or recovery of iron is a complex one with multiple steps [37,38]. Traditionally the initial refinement from ores is carried out via a pyrometallurgical process which relies on electrochemical recovery of iron as a secondary process[39]. However, the rapid advancement of the metallurgical industry led to the development of the so-called hydrometallurgical process, which involves iron electrodeposition directly via its roast-leach-electrowinning route[40]. This hydrothermal process has been shown to be able to treat lower ore grades while sustaining economic viability, reduce the direct carbon footprint and significantly lower the energy consumption (with reductions of up to 6 GJ/ton Fe)[41]. Depending on its final application, electrochemically produced iron is the main or only viable option due to very stringent requirements, such as those pertaining to purity, magnetic or chemical properties, or film thickness and structure, to name a few. Lastly, iron electrodeposition also plays a major role in selective recovery of metals, thus allowing a shift from a cradle-to-grave model in selective recovery of materials, therefore minimizing
environmental pollution and preserving natural resources. Various industries generate considerable amounts of iron-containing sludge or waste streams, such as steelmaking\cite{36}, formation and treatment of alloys and galvanization\cite{42}, or electronic scrap\cite{43}. In order for the recovered iron to be reintroduced into the market, the reclaimed metal needs to meet some quality criteria, such as purity or toxicity reduction, which can be reached via an electrowinning process while lowering the energy demand of primary material production\cite{42}.

Therefore, in this study we introduce a methodology to reliably compare and extract parameters that quantify the phenomena involved in hybrid solid-liquid iron batteries, namely plating nucleation, distribution and stripping behavior. Furthermore, we screen an array of additives of both organic and inorganic nature to gain insight into and tune the interaction of the iron ions and their electrodeposition behavior. Common requirements for additives in electroplating baths instruct that the selected molecules be common and cheap, in addition to being chemically and electrochemically resistant to reactions with iron ions or the iron anode\cite{44}. Some of the most used substances in plating baths are complexing agents based on acids. These usually act as buffering species, minimizing rapid or stark changes in electrolyte pH, by generating a more favorable nucleation energy barrier, and by decreasing or eliminating the precipitation of \ce{Fe(OH)_3} or \ce{Fe_2O_3}. Therefore, they can produce more uniform, compact, and fine grained plated layers. Accordingly, we selected three different multi-protic acid additives commonly used in iron plating cells, for increasing reduction strength, namely boric, citric and ascorbic acid. All three acids have been observed to partially inhibit the parasitic hydrogen evolution\cite{33,45,46}. Boric acid is one of the most often employed additives in aqueous electroplating baths, as it has shown local pH buffering and preferential adsorption of the borate complexes on the surface, thereby curtailing the formation of hydroxide layers and leading to increased nanocrystallinity\cite{47}. Metal citrates have also been observed to suppress simultaneous oxidation towards \ce{Fe^{3+}} ions and the reduction of protons, increasing cycling lifetime. For the specific case study of iron (II)-citrates, the complex has been postulated to create a solvation sheath coordination structure that preferentially leaves out \ce{H_2O} molecules\cite{46}. The low-spin configuration arising from the higher electron density of the 3D orbital of the \ce{Fe^{2+}} ion when partially bridged with citrates generates a preferential adsorption effect on the surface, hence modifying the nucleation and overall plating rates\cite{48}. In the case of ascorbic acid, the elimination of the aforementioned parasitic reactions has been previously reported to induce high
deposition performance and removal of amorphous features[49]. Furthermore, citrates and ascorbates can increase the solubility of iron in the entire range of acidic pH[33]. Specifically iron-ascorbates display a low spin configuration, increasing the reversibility of plating due to the low splitting energy of the ligand when applying the reductive potentials characteristics of charging[50]. Other types of additives, such as levelers or surfactants are common amongst electroplating additives. The former are posed to accelerate the growth of highly reactive metals whilst minimizing the concentration of metallic ion needed at the surface. This is the case of thiourea, frequently used in other battery chemistries, which has been shown to lower polarization overvoltages and increase cycling stability due to the pseudo-catalytic properties of the sulfide-conjugated bond, which suggest accelerated nucleation behavior[51,52]. In the case of surfactants, such as the selected tetrabutylammonium chloride (TBACl), we hypothesize that could aid as a wetting agent and help in the ion replenishment process, helping control selective oxidation or pitting[45,52]. We hypothesize that, due to the structure of TBACl, with a hydrophobic long chain, and a positively charged head, the positive iron ion could only be transported to the surface trapped among the long hydrophobic chains, thus controlling the release rate of ions to the surface and promoting the formation of thin, even layers. Whilst this may result in a reduced number of nucleation atoms, it could in turn lead to finer grain sizes and reduced amount of free volume in the deposited layers that aid in avoiding capacity decay and greater cycle life[53].

In this work, we used a variety of techniques to systematically study the formation, growth and dissolution of metallic iron: firstly, we performed a chronoamperometric nucleation analysis over a range of overpotentials practical for AIB operation (50 – 1000 mV), and we then analyzed the normalized current transients. We hypothesize that, by employing a number of selected additives and performing a systematic single-step deposition reaction, we can tune and deconvolute the nucleation processes to produce more homogeneous and better structured coatings with improved energy optimization, to later leverage battery performance. Subsequently, we adapted analytical models to account for the iron electrodeposition process with simultaneous hydrogen evolution, and we deconvoluted the partial plating currents, plating kinetics and spatial distribution, in addition to hydrogen evolution kinetics and their dependence with electrolyte composition and cell overvoltage (Figure 1a) in a symmetric Fe$^{2+}$|Fe$^{0}$ cell (Figure 1b). Thereafter, we determined the resulting electrode surface and crystallographic structure with
microscopy and x-ray diffraction analysis. Finally, we examined the performance of the electrolytes in *symmetric* configuration as a proxy for cyclability (Figure 1c). Through these techniques, we found that the aforementioned additives (Figure 1d) allow superior plating cycling due to their balance between nucleation enhancement and epitaxial electrodeposition with HER suppression. In summary, our aim is to develop a methodology for accurately screen electrolytes and electrode materials and enable deconvolution of relevant physical parameters to help understand plating phenomena. We hope that these findings will help design flow battery electrolytes with improved performance and durability.
2. EXPERIMENTAL

2.1. Chemicals and Materials

All chemicals were used as received without further purification. Iron (II) chloride tetrahydrate (FeCl$_2$·4 H$_2$O 99%, 1 M), hydrochloric acid (HCl ACS reagent 37%, 1 M), boric acid (ACS reagent 99.97%), ascorbic acid (ACS reagent 99%), thiourea (ACS reagent 99%), and tetrabutylammonium chloride (TBACl, reagent grade 97%) were purchased from Sigma Aldrich. Citric acid (AnalaR NORMAPUR 99.9%) was purchased from VWR Chemicals. Ultrapure water (ELGA PURELAB) 18 MΩ was employed for all solutions.

Commercial iron films were used as the electrode material (25 µm thickness, 99.5 % purity, GoodFellow GmbH). Polymer-infused graphite rods (G347B graphite, MWI Inc) were designed and machined in house (22.3 mm in height, 12.7 mm in diameter) and used as current collectors in the employed perfluoroalkoxy (PFA) Swagelok™ type cell.

2.2. Chronoamperometric iron electrodeposition study

The first stage of our study was to assess the nucleation and electrodeposition behavior of iron (II) in aqueous baths towards their optimization when used in iron batteries. Common operation specifications require the batteries to be operated at high or fluctuating current densities, which can give rise to uneven structures and composition of the plated layers incompatible with extended operation.

Firstly, the electrodes were cleaned with 0.1 M HCl to remove native oxides or carbonates that might have been formed during the manufacturing process, as they would enhance uneven current density distribution. They were additionally degreased with acetone and rinsed abundantly with ultrapure water after each cleaning step.

We performed the electrodeposition of the studied iron layers on the cleaned and degreased commercial iron films from deaerated, acidic baths of iron (II) chloride, with or without the presence of additives. We studied the electroplating process via chronoamperometric (CA) reduction at room temperature, with stagnant electrolyte, in a two-electrode PFA Swagelok™ type cell with polymer graphite current collectors, as described elsewhere[54,55]. The specific
design of the cell used in this work can be seen in Figure 1b. This Swagelok™ cell consisted of a 2-sided, bored-through ½ inch (outer diameter) tube fitting, with an internal volume of 540 µL and tightened to 6 N m torque. The composition of the electrolytic baths with different additives is compiled in Table 1. For the electrolytes containing boric, citric and ascorbic acid, respectively, their concentration was kept at 10% of the concentration employed for FeCl₂, as it has been reported to be optimal to ensure complete solubility in the negative electrolyte and as a stabilizing agent[15,56]. The additive concentration was reduced in the electrolytes containing thiourea and TBACl due to differences in solubility limits in aqueous solutions. Additional plating experiments were carried out at HCl concentrations of 2, 1, 0.1, 0.01 and 0.001M without the use of additives, (see Table 2) to observe the effect of different electrolyte pH. In all cases, operating potentials comprise 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1 V, for a duration of 10 seconds, with a sampling time of 20 ms. Both working and counter electrodes were commercial iron foils of high purity (vide supra), of circular shape and 1 cm diameter (exposed area). All measurements of electrode preparation were performed in triplicates for individual samples new assemblies and at room temperature.

Figure 1. Schematic representation of the outline of this manuscript. (a) Experimental and analytical study of the influence of electrolyte additives on the behavior of iron
electrodeposition, with focus on the kinetic parameters of single-step electroplating (b) Cross section of the 2-electrode, stagnant Swagelok™ type cell used for the iron electroplating studies. (c) Study of the influence of electrolyte additive on overall cycling performance of a symmetric Fe^{2+}/Fe cell and (d) Electrolyte additives and HCl concentration studied in this manuscript (see Tables 1 and 2 for electrolyte compositions).

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<td>Tetrabutylammonium Chloride</td>
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Table 1. Composition of baths employed in the iron electroplating experiments with additives. Concentrations of FeCl₂ and HCl were 1 M, and kept constant for all experiments.

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<th>[HCl] (mol dm⁻³)</th>
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Table 2. Composition of baths employed in the iron electroplating experiments as a function of pH. Concentrations of FeCl₂ was 1 M and kept constant for all experiments, without addition of additives.
2.3. Morphological and crystallographic analysis

The surface morphology of pristine and additive-assisted coated iron electrodes was examined by a JEOL JSM-IT100 a scanning electron microscope (SEM) at 20 kV acceleration voltage, with a probe current of 30 and a working distance with the stage of 10 mm. X-Ray diffraction (XRD) spectra of the samples were collected using a Rigaku MiniFlex 600 X-ray benchtop diffractometer. The samples were analyzed at power of 600 W, 40 kV acceleration voltage and 15 mA applied current, in the 2-0 range of 2-120° with a 0.02° degree step and 4° min⁻¹ sweep rate. The employed target was copper Kα, with a wavelength of 1.54056 Å. The built-in Rigaku PDXL Analysis Package was employed for noise reduction, background elimination and peak search and match with the ICDD-PDF (International Center for Diffraction Data – Powder Diffraction File) databases. The observed surfaces for SEM and XRD characterization correspond to the side facing the electrolyte compartment of the working electrodes (cathodes) after single-step CA deposition for all samples, see Figure 1b. The samples were analyzed as-deposited and did not require any further preparation.

2.4. Battery cyclability measurements

Single-step CA nucleation analysis can enable comparative analysis for the different electrolyte compositions and begin to shed insight into the fundamentals and optimization of the electrodeposition process [57,58]. However, this technique would not be representative of practical battery operation, where deposition and stripping are expected to take place repeatedly, which could exacerbate deposition inhomogeneities, further limiting efficiency and lifetime. To account for the effects of the consecutive deposition and stripping (as a proxy for the charge and discharge processes in a full battery), we carried out additional cyclability measurements in symmetric cell configuration. We performed said experiments in Swagelok™ type cells as described above via a galvanostatic charge-discharge technique, performed at a constant rate of 35.7 mA g⁻¹ and 0.6 C, with cut-off voltages of +/- 0.2 V (Figure 1c). Electrochemical impedance spectroscopy was recorded at open circuit potential, in the frequency range of 500 kHz to 200 mHz, with a sinus amplitude of 10 mV, with 8 points per decade, 6 measurements per point, and a waiting time of 0.10 before each frequency. All measurements of
electrochemical characterization were performed in triplicates for new assemblies and at room temperature.

3. RESULTS AND DISCUSSION

3.1. Chronoamperometric iron electrodeposition study

To understand and optimize the mechanism of electroplating, we employed a series of reductive potentiostatic steps, proven to be a robust technique to elucidate the formation of metallic phases during electrodeposition[57,59,60]. Our experimental chronoamperometric results prove to be quite stable, thus allowing further theoretical nucleation analysis; an extract of the obtained data for the CA study can be seen in Figure 2 where the baseline electrolyte and the boric acid-modified electrolyte are shown, at 50 and 800 mV. The rest of experimental results for the CA studies are compiled in Figure S1. All collected data was fitted in the form of current-time transients to determine and quantify the type of nucleation process taking place. As data was obtained in a 2-electrode configuration, the chronoamperometry nucleation results will refer to a hybrid process that includes global information of both anodic and cathodic Fe$^{2+}$/Fe$^0$ processes. However, as has been observed previously, iron plating and stripping are highly asymmetrical processes with distinct charge transfer coefficients[61,62]. As a result, the iron plating reaction dominates the overall process where the H-bonding network of the solvent with Fe$^{2+}$ notoriously affects the already poor reversibility[63]. This in turn results in overpotentials that comprise up to 80% of the cell’s total overpotentials due to the greater energetic barrier for Fe$^{2+}$ desolvation and Fe nucleation[48,64]. Therefore, in the following sections, we assumed that the global cell voltage and current density were mainly attributed to the iron reduction reaction and thus, were used to deconvolute and quantify the nucleation mechanism of iron plating.
Figure 2. Experimental data for the chronoamperometric iron deposition studies at two sample voltages. (a) 50 mV and (b) 800 mV. Graphs show results for two electrolyte compositions: BE baseline electrolyte containing FeCl$_2$ 1 M, HCl 1 M [black line, ——], and the modified electrolyte containing FeCl$_2$ 1 M, HCl 1 M and boric acid 100 mM [red line, ——]. Solid lines represent current density averages for the triplicate experiments and shaded area represents the 99% confidence region. The results for the remaining voltages and electrolyte composition studies can be seen in Figure S1.

3.2. Analytical models of plating

In order to evaluate the influence of the selected molecules and their effect on the nucleation and plating process, we performed a numerical analysis to elucidate the type of mass transfer and associated nucleation process within the framework of macroscopic analytical modeling. This first analytical evaluation allows us to then estimate specific nucleation descriptors, such as nucleation rate, and nucleation center distribution through more detailed nucleation models.

As a first consideration often overlooked in the literature, we will first describe the simultaneous reduction processes taking place in the negative half-cell of iron batteries during charge. In this compartment, the iron electrodeposition (FeED) and the hydrogen evolution reactions (HER) (R1 and R2, respectively), always occurs simultaneously due to the substantial overlap in reduction potentials:

\[ Fe^{2+} + 2 \, e^- \rightleftharpoons Fe^0 \quad E^0 = -0.440 \, V_{SHE} \]  \quad (R1)

\[ 2 \, H^+ + 2 \, e^- \rightleftharpoons H_2 \quad E^0 = 0.00 \, V_{SHE} \]  \quad (R2)
Consequently, both FeED and HER have to be considered, not only when analyzing their determining effects on the morphology and surface properties of the plated layer, but also when performing modeling or parameter determination.

Initially, we explored a chemically agnostic model that relies primarily in the mass transfer properties of the system. In accordance with the current-time transients (Figure 2 and Figure S1), two main tridimensional nucleation mechanisms can take place, instantaneous and progressive, equation (1) and equation (2), respectively, defined by the Scharifer and Hills (SH) model[60,65,66].

\[
\left(\frac{i(t)}{i_{\text{max}}}\right)^2 = 1.9542 \left(\frac{t_{\text{max}}}{t}\right) \left(1 - \exp\left(-1.2564\left(\frac{t}{t_{\text{max}}}\right)\right)\right)^2 \tag{1}
\]

\[
\left(\frac{i(t)}{i_{\text{max}}}\right)^2 = 1.2254 \left(\frac{t_{\text{max}}}{t}\right) \left(1 - \exp\left(-2.3367\left(\frac{t}{t_{\text{max}}}\right)^2\right)\right)^2 \tag{2}
\]

where \(i(t)\) is the current density measured for electrodeposition at a given time, \(t\), \(i_{\text{max}}\) is the maximum current density measured for each case study occurring at \(t_{\text{max}}\). A sharp increase can be observed until \((t_{\text{max}}, i_{\text{max}}, \text{see Figure 3a and Figure S1})\), due to a reorganization of ionic and solvent species at the electrode and subsequent nucleation. The nucleation and growth of nuclei would take place independently until \(t_{\text{max}}\), where diffusion boundary layers begin to overlap. This is followed by an exponential decrease followed by a plateau, which could be an indication of ion depletion and generation of a linear diffusion layer of \(\text{Fe}^{2+}\) ions in the proximity of the electrode surface.

In Figure 3, the normalized current transients, \(i/i_{\text{max}}\) vs \(t/t_{\text{max}}\) are represented, comparing experimental data to the theoretical behavior described by equations (1) and (2). The experimental data displays the shape of a process of metallic new phase formation via multiple nucleation, with mass transfer controlled hemispherical growth and the additional reduction process, HER in this case, in accordance with previous research[58,65]. For all studied cases before reaching \(i_{\text{max}}\), experimental data adheres better to the instantaneous nucleation model, albeit it does not display a complete match to this mechanism. As nucleation and electroplating progress, it is expected that the dimensionless current density would decrease sharply in log-
normal fashion[58,60,67]. However, for values of normalized time above unity, more noticeable deviations in normalized current density are observed, where the evolution of experimental $t/t_{max}$ follows more closely the progressive nucleation behavior. Nevertheless, large discrepancies are still observed in this region, which could be attributed to two main factors. Firstly, the nucleation of iron species does not follow the instantaneous or progressive model accurately, which correspond to immediate nucleation ($t_{nuc} \rightarrow 0$) on a finite number of active sites versus progressive seeding on an infinite number of sites. An intermediate case would rather imply progressive nucleation on a fixed number of active sites. Therefore, it can be inferred that this system follows a three-dimensional progressive nucleation phenomena where the generated nuclei grow limited by the diffusion control of species[58]. Additionally, the faradaic inefficiencies introduced by electrolyte degradation occurring concurrently with the plating process, which is not captured by the SH equations, are seen in the large discrepancies at high $t/t_{max}$ between the dimensionless current densities in Figure 3a.
Figure 3. Model fitting to experimental data for chronoamperometric iron electrodeposition. (a) Scharifer-Hills (SH) model, normalized current-time transients. Graphs show experimental data [black line, ——], theoretical instantaneous mechanism (equation (1)) [red line, ——] and progressive mechanisms (equation (2)) [blue line, ——]. (b) Palomar-Pardavé (PP) model, best-fit current transient; graphs show the experimental current density data ($i_{\text{exp}}$) [black line, ——], theoretical partial current density for iron plating ($i_{\text{FeED}}$) [red line, ——], theoretical partial current density for hydrogen evolution reaction ($i_{\text{HER}}$) [blue line, ——] and theoretical total current ($i_{\text{model}}$) [green line, ——]. All experiments refer to deposition using the baseline electrolyte, BE, containing 1 M FeCl$_2$, 1M HCl. Results for electrodeposition at two sample voltages are shown: top: 50 mV and bottom: 500 mV.

Taking the above factors into consideration, and in order to systematically quantify electrodeposition descriptors, the model by Palomar-Pardavé[68,69] was adapted to the iron chemistry, to illustrate nucleation on a finite number of plating seed sites, with diffusion-dominated growth of the plated layer and simultaneous proton reduction:
\[ i(t) = i_{FeED}(t) + i_{HER}(t) = \left( P_1 + \frac{P_3}{\sqrt{t}} \right) \left( 1 - \exp \left( -P_2 \left( t - \frac{1 - \exp(P_3 t)}{P_3} \right) \right) \right) \] (3)

Where

\[ P_1 = \left( \frac{2 C_b M_W}{\pi \rho} \right)^{1/2} z_{HER} F k_{HER} \] (4)

\[ P_2 = N_0 \pi D_{eff} \left( \frac{8 \pi C_b}{\rho} \right)^{1/2} \] (5)

\[ P_3 = A \] (6)

\[ P_4 = \frac{z_{FeED} F C_b D_{eff}}{\pi^{1/2}} \] (7)

where \( C_b \) is the bulk concentration of Fe\(^{2+}\) ions, \( M_W \) is the iron molecular mass, \( \rho \) is the density of the metallic deposit, \( F \) is Faraday’s constant, \( z_{HER} F \) is the molar charge exchanged during the proton reduction reaction, \( k_{HER} \) is the electrochemical reaction rate of HER, \( D_{eff} \) is the effective diffusivity of Fe\(^{2+}\) ions in the electrolyte, \( A \) is the nucleation rate for electrodeposited iron per active site, \( N_0 \) is the superficial density for iron electrodeposition on the substrate, and \( z_{FeED} F \) is the molar charge exchanged during the iron electroplating reaction. Fitting the experimental data to the model described by equation (3) was performed via the least-squares curve fitting Levenberg-Marquardt algorithm. Parameters obtained from the best fit iteration are summarized in Tables S1 – S6. Thereafter, the partial contribution to the global current density of both HER and FeED reduction processes is obtained and the theoretical total current is compared to the experimental value, showing good correlation between them (Figures S2 – S7).

### 3.3. Influence of additives on iron electroplating performance

For optimal battery operation and industrial applications of electroplated iron, metal plating is expected to take place creating hemispherical or, preferentially, planar structures, as opposed to branched-out structures characteristic of mass transfer limited regimes, which can potentially lead to passivation or battery failure[34]. Specifically, these preferred structures arise when the nucleation seeds are very abundant and broadly distributed over the working surface, thus consolidating a more coherent and better packed plated structure.

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Consequently, the analysis described above was systematically performed for all studied electrolytes (for compositions, refer to Table 1) in order to determine which additive provides the best overall properties, and iron plating-related kinetic parameters in particular, towards optimization of AIBs. For such systems, the control of operating parameters such as pH is crucial towards stable operation, management and regulation of the electrodeposition. Defining an optimal pH value is an arduous task, as it is highly dependent on the system and final application and its requirements. Particularly for iron plating, the reported range of used pH in the literature comprises pH 0 and below for continuous operation, which aids with limiting concentration gradients towards the electrode surface during the reductive process [70–72] up to values of around 3, which is the upper boundary of the operation window to avoid oxidative precipitation of ions [17,56,72]. For all pH values there will be a trade-off effect between the faradaic losses introduced by the acid content and with stability of the electrolyte composition and losses of active material. Although this work does not seek to find an optimized pH, we briefly evaluate the effects of acid content on the overall reduction process and the individual FeED and HER reactions (refer to section S3.7 of the Supporting Information). Based on our finding, we selected a concentration of HCl 1M as supporting electrolyte, as we found that this can support adequate current densities for plating and has superior charge carrying capacity, lowering concentration and migration overpotentials, therefore relying on additives to optimize the process efficiency.

Following the parameter fitting of the experimental data to equations 3 – 7, we performed a deconvolution of the partial plating currents, depicted in Figure 4 (red line in Figures S2 – S7). The plating current density follows a similar evolution with respect time to the global current density (black line for total experimental in Figures S2 – S7) for all electrolyte compositions: an initial peak followed by an exponential descent which we attribute to species depletion near the electrode surface, whereas the current associated with HER (blue lines in Figures S2 – S7) remains high all throughout the studied potential interval due to the excess species introduced by the solvent. We observed that for all electrolyte compositions, the contribution of the iron electrodeposition reaction is nearly negligible at low potentials, up to 100 mV, as the system has likely not yet fully surpassed the energetic barrier for practical electrodeposition[68]. Starting at 200 mV, plating current densities become significant and three different trends ensue. For electrolytes without additives, or with boric, citric or ascorbic acid, the current density keeps increasing halfway through the studied potential range, until 500-600 mV, after which there is a
general decay due to the exponential increase in HER kinetics, as seen below in section 3.4. The plating process with thiourea-containing electrolyte displays a continuous, exponential increase, reaching the highest plating rate of all studied electrolytes, up to reach a nearly 100% increment compared to the baseline, unmodified electrolyte (of about $i_{FeED}(max) \sim 25 \text{ mA cm}^{-2}$ for the baseline electrolyte versus $i_{FeED}(max) \sim 50 \text{ mA cm}^{-2}$ for the electrolyte with thiourea). Lastly, the TBA electrolyte renders moderate current densities until about 500 mV, after which it experiences a noticeable increase, with nearly constant current density at higher potentials. When factoring in the contribution by electrolyte degradation, we observe that all employed acids cause increases in faradaic efficiency (Figure 5) all across the studied voltage range, with improvements up to 25%.

This signifies that the major effect of these substances is by reducing the undesired proton reduction reaction, but with also an influence on the mechanism of iron plating. The TBA electrolyte follows a similar trend in terms of current efficiency, although in lower magnitude at the lower and higher ends of the studied voltage range (Figure 5a vs 5d). This, in conjunction with the different evolution of current density (Figure 4d) seems to indicate a different mechanism or interaction taking place between the additive and the active species. The largest difference in efficiency evolution is seen for the thiourea electrolyte, as it tends to oscillate around 40%. This would entail not only enhanced reaction rate for plating, but also hydrogen evolution.

To elucidate the mechanisms behind these behaviors, we obtained relevant nucleation parameters from the data in Tables S1 – S6. With the best-fit parameters obtained from the experimental data and equation (3), we deconvoluted these parameters into iron nucleation rate ($A$) and nucleation center density ($N_0$) (equations 4 to 6). Similarly, we studied the competing HER via analysis of its kinetic constant ($k_{HER}$) (equation 7), see section 3.4. The dependence of $A$ and $N_0$ to increasing potential for all studied compositions is depicted in Figure 6. When studying the kinetics of iron nucleation we note that the nucleation rate follows a sigmoidal evolution. All additives caused a sharper increase at lower potentials compared to the unmodified electrolyte case, plateauing around the value of 1 $\text{s}^{-1}$, whereas thiourea and TBACl remain around 0.8 $\text{s}^{-1}$. The values of the nucleation center density (Figure 6, empty symbols with cross), also rise with increasing overpotential. In the case of additives b-d, that is, the acid-derived buffering agents.

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the increase is greater than in case of the non-modified electrolyte (Figure 6a), whereas the increments are much more moderate for thiourea and TBACl (Figure 6e and f, respectively), that is, nucleation is more constrained over the available electrode surface.
Figure 4. Voltage and time dependence of theoretical current density for iron electroplating between 50 and 1000 mV applied deposition overpotential for (a) the baseline electrolyte containing FeCl₂ 1 M and HCl 1 M, and (b-f) modified electrolytes: (b) electrolyte containing FeCl₂ 1 M and HCl 1 M and boric acid 100 mM, (c) electrolyte containing FeCl₂ 1 M and HCl 1 M and citric acid 100 mM, (d) electrolyte containing FeCl₂ 1 M and HCl 1 M and ascorbic acid 100 mM, (e) electrolyte containing FeCl₂ 1 M and HCl 1 M and thiourea 100 ppm, (f) electrolyte containing FeCl₂ 1 M and HCl 1 M and TBACl 100 ppm.
Figure 5. Faradaic efficiency dependence with potential for iron electroplating between 50 and 1000 mV applied deposition overpotential for (a) the baseline electrolyte containing FeCl$_2$ 1 M and HCl 1 M, and (b-f) modified electrolytes: (b) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and boric acid 100 mM, (c) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and citric acid 100 mM, (d) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and ascorbic acid 100 mM, (e) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and thiourea 100 ppm, (f) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and TBACl 100 ppm. Dotted lines represent interpolated trends to guide the eye.
3.4. Influence of additives on HER suppression

Related to the variations in iron plating parameters studied above, we then proceed to evaluate the impact the different additives on the suppression of the parasitic hydrogen reaction. Uncontrolled HER can negatively affect the changing electrode morphology during the plating-stripping stages and energy utilization, thus leading to decreased flow battery performance. Therefore, we analyzed the impact that the selected additives had on the HER rates, more
specifically, on its kinetic constant, via application of equations 3 and 4 derived from the Palomar-Pardavé model above, to the experimental CA data.

It was found that the kinetic constant for proton reduction, $k_{HER}$, follows an exponential, Arrhenius type evolution with potential[73] (Figure 7) for all electrolyte compositions, with the greatest changes observed after 600 mV, notably for electrolytes the baseline electrolyte and those containing boric, citric, ascorbic acid and TBACl). Despite this increase, we observed that the $k_{HER}$ value for electrolytes with acids and TBACl remained at all times lower than the baseline electrolyte without additives. The particular structure of the cationic surfactant TBACl, can cause specific effects during the mass transfer and deposition steps. We estipulate that the external non-polar groups generate a ferrophobic repulsion mechanism with simultaneous inner adsorption of Fe$^{2+}$ with the polar end of the chain. The long non-polar segments would form chain-chain interaction with ion-phobic properties[74]. Accordingly, new solvated, polarized Fe$^{2+}$ will be redirected towards adjacent, unplated regions, allowing for the formation of thinner, smoother and more compact layers[74]. Although this mechanism limits the formation rate and density of nuclei at a given time, as seen above in Figure 6a, the lateral diffusion of the Fe-TBA$^*$ radical species occurs fast enough that global nucleation and growth current density are not largely affected. Simultaneously, the long chain interactions induce a loss of hydrophilicity, that can shield proton access to the proximity of the electrode active sites, thus reducing the HER electrochemical rate constant ($k_{HER}$) and boosting the faradaic efficiency (Figure 5a vs 5f).

For thiourea, however, we note that $k_{HER}$ remains higher than the baseline electrolyte until 500 mV, after which it begins to increase at a lower rate than the rest of cases. Previous studies postulate that this behavior is characteristic of a system where nucleation is heavily segregated within certain regions of the electrode surface, and plating coverage occurs primarily due to electrodeposited seed growth[75]. We later confirmed this behavior via SEM imaging (see Figure 8e), where the plating appeared to have taken place in preferential hemispherical deposits of varying size distributed over the entire working electrode are. Consequently, despite the suppressing function of thiourea towards side reactions, we theorize that this effect is not actively displayed until a threshold potential or charge are reached to grant a sufficient degree of surface coverage for the electroplated iron[76]. This could also be attributed to the fact that, mainly at low to mid potentials, thiourea promotes the adsorption of hydrogen ions, due to their
affinity towards the electron pairs of the N and O atoms, while simultaneously regulating density of the deposit, as it induces a superfilling effect at the microscopic level[77]. This additive is usually regarded as an accelerator for various types of metal plating processes, which benefits from the conjugated effect of the thio- function - the extended C=S covalent bond and the dispersed π bond between the sulfur, carbon and nitrogen atoms, can lead to increased charge transfer processes for metal electroplating, actively altering the kinetics process[78]. Thus, both HER and iron electrodeposition reactions can be enhanced overall, although, this is at the expense of limiting the nucleation process. The increased hydrogen evolution reaction limits the available surface area available for nucleation, severely curtailing nuclei density and rate, as seen in Figure 6e. Since these complexed units do not support drift or lateral diffusion on the electrode, this translates into surface segregation on areas where HER occurs preferentially throughout the reduction process, and areas for preferred electroplating, where the restrained nucleation forces a more tridimensional growth perpendicular to the substrate.

The studied acid additives (b-d) have been previously found to form complexes with metallic ions that adsorb on the surface thereby altering and regulating the desorption mechanism and rate of iron ions preceding nucleation and electrocrystallization[79]. These complexed iron units are more easily adsorbed onto the surface due to the presence of the polar moieties and pi-orbital electrons of the additives[78]. Upon coordination, the activation energy of the complexed iron increases for both anodic and cathodic reactions. This translates into supersaturation of the iron-complex adatoms (adsorbed atoms). This requires an additional step of decomplexation in the process of electroplating. Based on the previous results pertaining to plating current deconvolution, we can assume that this decomplexation occurs in a relatively fast fashion[23]. Consequently, this majorly preserves the iron plating rate (Figure 4 b-d) while effectively blocking access of protons to the surface and therefore increasing the overall faradaic efficiency. The resulting structures are preferentially planar as this hinders radial growth of the deposited layer and promotes flatter structures over tridimensional ones. Consequently, this results in increased nucleation density and finer crystal size, as opposed to growth of few, individual crystals, creating more compact layers with better coverage[80], see Figures 8 and 9.

Boric and ascorbic acids additionally serve as strong reducing agents curtailing the formation of ferric ion. Accordingly, this eliminates an additional layer of inefficiency pertaining to ferric-
ferrous ion conversion or formation of ferric-oxo or ferric-hydroxide species, which form an unstable solid-electrolyte interphase (SEI) like layer of reduced electronic conductivity upon cycling[81].

Figure 7. Voltage dependence of hydrogen evolution reaction kinetic constant during iron electrodeposition for (i) the baseline electrolyte containing FeCl$_2$ 1 M and HCl 1 M, and (ii-vi) modified electrolytes: (ii) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and boric acid 100 mM, (iii) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and citric acid 100 mM, (iv) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and ascorbic acid 100 mM, (v) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and thiourea 100 ppm, (vi) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and TBACl 100 ppm. Dashed lines show interpolated trends.

Additionally, and from a structural point of view, we hypothesize that the adsorption of these surface agents can inhibit the formation of crystallographic planes with lower Miller indexes, which are more reactive and unstable. The differences in surface reactivity for these types of crystal planes have been attributed to the formation of crystallite dislocation etch pits and dislocations in the grain border structure[82]. On these, reactions involving liquid-gas conversions such as HER have been observed to be favored due to the lower thermodynamic barrier for gas nucleation, consistent with the extensively studied Gibbs-Thomson phase
transformation effect[83,84]. Accordingly, the studied chelating effect will reduce the parasitic hydrogen evolution reaction in a two-fold fashion: the preferential adsorption of the chelates will block access of protons to the active sites, and the remaining available sites will display reduced reactivity toward their reaction, thus reducing the electrochemical rate constant for HER across the voltage range, as can be seen in Figure 7. This is in accordance with the increased plating current efficiencies and nucleation rates (see Figure 5 and Figure 6) for these modified electrolytes, which derives in higher charge/discharge round-trip efficiency[85].

3.5. Morphology and crystallography of the electroplated layers

After quantitatively analyzing the effects of all additives on the kinetic-related parameters and studying the potential changes in the reaction mechanism, we then correlated these effects on the resulting electrode morphology and microstructure via SEM imaging (Figure 8) and XRD analysis (Figure 9).

Figure 8 displays the resulting morphology of the iron electrodes after the single-step chronoamperometric deposition at the potential that yielded the peak faradaic efficiency for each electrolyte (cathodic WE, surface facing the electrolyte chamber, see Figure 1b) at different magnifications (x250 and x10,000) to show the main structural features of the plated layers. We find prominent differences in resulting microstructure across the studied surfaces. Firstly, the pristine iron foil (Figure 8) surface is shown to be flat and relatively smooth, although some scratches and minor grooves are present, likely originating from the manufacturing process. It must be noted that the present microscopic gaps on the surface can induce poorer wettability between electrode and electrolyte.
Figure 8. Scanning electron micrographs of (Ø) the pristine iron substrate, and after electrodeposition at peak plating efficiency with (a) the baseline electrolyte containing FeCl$_2$ 1 M and HCl 1 M, and (b-f) modified electrolytes: (b) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and boric acid 100 mM, (c) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and citric acid 100 mM, (d) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and ascorbic acid 100 mM, (e) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and thiourea 100 ppm, and (f) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and TBACl 100 ppm. x250 (1) and x10,000 (2) magnifications are shown.

The deposition of iron from the baseline electrolyte containing no additives (Figure 8a) results in a hybrid structure, consisting of island-like regions combined with the formation of needle-shaped dendrites of 100-200 nm in size. The use of the studied additives exhibit a distinct improvement in surface morphology, with pronounced mitigation of dendrite formation or irregular structures. For the iron borate, citrate and TBA-complex (Figure 8b, 8c and 8f), we observed an increasing smoothening of the surface. We attribute this to the influence of the decomplexation step prior to iron deposition, thus obstructing the free growth directions and the hydrogen evolution reaction, which not only causes energetic losses, but also aggravates dendrite generation and inhomogeneities in voltage fields[86]. The decomplexation step would occur at different rates, resulting in slight changes in morphology. In the case of the plated layer with the borate additive, small columnar artifacts are observed, on a majorly smooth surface. Citric acid-containing electrolyte displays a similarly smooth layer, albeit with fewer protrusions and reduced height. For TBACl, the resulting structure is mostly flat with sparse dents likely arising from the localized hydrogen evolution reaction. We observed more notable structural changes for the anode modification with thiourea (Figure 8e), as iron is primarily deposited in elevated, hemispherical structures spanning 30 to 150 µm. This behavior is characteristic of a system
where nucleation takes place in a segregated manner, as hypothesized above, thus justifying the more prominent HER suppression at mid-to-high voltages when the growth of the limited nucleation seeds becomes more significant (see Figure 6e and Figure 7e). However, this electrode presents a lengthwise flaky morphology with small pits at the nanoscale, which we attribute to the increased current densities generated (Figure 4e), which accentuates ion depletion by the electrode surface. Nevertheless, the electrodeposition process does not fully reach the undesired diffusion controlled region that would cause dendritic deposition (as is the case of the electrolyte with no additive, Figure 8a) due to thiourea’s superfilling effect[77]. This effect could cause the thiourea electrolyte to likely remain in a mixed controlled regime, comprised between planar and dendritic deposition, see Figure 10 for distribution of the plating regimes as per their electrochemical to self-diffusion ratio. Lastly, the layer plated with ascorbic acid (Figure 8d) shows bigger protrusions in the micrometer range, with distributed presence of oxides in the structure, as later corroborated by XRD analysis (Figure 9d). This would indicate that the ascorbate is not successful enough at avoiding hydrolysis of \( \text{Fe}^0(s) \rightarrow \text{Fe}^{3+} \) with subsequent precipitation.

In addition to the surface characteristics of the plated electrodes, their crystalline structure can be critical in defining their battery performance. Figure 9 shows the X-ray diffraction spectra of the studied samples. All specimens show the characteristic peaks (1 1 0), (2 0 0) and (2 1 1) of pure metallic iron[48]. However, some display additional features around the value of 22° for 2-θ, which corresponds with the presence of FeO and Fe₂O₃ species[64]. These appear, as expected, predominantly in the untreated iron substrate as the native oxides generated during the manufacturing process, and are notably enhanced in the ascorbate-assisted deposition, in agreement with the observations previously made in the micrographs compiled in Figure 8. For the main iron peaks, there is no significant shift in the 2-θ value, although the intensities of the difference facets vary, indicating prevalence of the different planes. Planes with lower crystallographic indexes such as (1 1 0) have been shown to have higher intrinsic reactivity, mainly towards HER, which generates the most irregular deposits. The highest relative intensities of (1 1 0) can be seen for the untreated substrate, but are substantially increased in the electrodes plated with the non-modified baseline or the ascorbate-containing electrolytes. This can be attributed to a number of phenomena. Firstly, this would be in agreement with our previous observations where mode abundant low crystallographic indexes are linked to enhanced...
HER kinetic rates (see Figure 7). This can be directly correlated to the formation of dendrites or oxides in directions perpendicular to the electrode surface. Additionally, other phenomena can arise, such as spontaneous corrosion and self-discharge, that is, morphological and electrochemical degradation (Figures S8 and S9), as observed in the present and previous works[21,55]. Conversely, the presence of all other additives in the plating solution managed to suppress growth on the (1 1 0) direction to different extents, instead favoring growth towards (2 0 0) and (2 1 1), which decrease progressively in thermodynamic reactivity. The greater intensity of these reflexion planes with increasing Miller indexes are able to sustain more nucleation sites (Figure 4 and 6) and planar rotational alignment, hence improving battery cyclability[87], as seen in Figure 11. We hypothesize that the controlled release of Fe$^{2+}$ by chelate decomplexation and the restriction of free growth promotes the formation of layers with basal growth instead, with a reduction in grain size and increased densification and uniformity of the deposits. These latter planes have been observed to reduce degradation of the electrodes by uncontrolled, localized corrosion, or self-discharge of metallic anodes (Figure S9).
**Figure 9.** X-ray diffraction spectra comparison of the pristine commercial iron foil and electrodeposited iron layers with (a) the baseline electrolyte containing FeCl$_2$ 1 M and HCl 1 M, and (b-f) modified electrolytes: (b) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and boric acid 100 mM, (b) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and boric acid 100 mM, (c) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and citric acid 100 mM, (d) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and ascorbic acid 100 mM, (e) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and thiourea 100 ppm, and (f) electrolyte containing FeCl$_2$ 1 M and HCl 1 M and TBACl 100 ppm.
3.6. Surface regimes of electroplated layers

As observed above, the composition of the electrolyte governs the different reaction rates taking place within the cells, and in turn affect the structure and morphology of the electrodes. As such, these changes can contribute to the different types of cell overpotential and overall cell performance. When these kinetic rates compete with diffusion rates in the electrolyte bulk, within the double layer region or, more critically, with the self-diffusion rate at the very electrode surface, we enter a deposition regime of severe mass-transfer limited growth[88–90]. Therefore, it is relevant to develop a relationship that allows us to correlate the balance between the electrodeposition reaction and the diffusion rate, in order to predict variations of the surface structure and morphology (Figure 10).

To evaluate the effect of this charge transfer versus mass transfer regimes, we can express the ratio between metal ion depletion by electrochemical reaction ($k_e$) and its diffusion rate on the surface ($k_{diff}$) as the dimensionless Damköhler ($Da$) number:

$$Da = \frac{k_e}{k_{diff}}$$  \hspace{1cm} (8)

where $k_e$ is assumed to be equal to $A$ for the initial 10 seconds of electrodeposition that have been analyzed (Figure 2 and Figure S1), assuming nucleation dominates over general deposit growth, and $k_{diff}$, a measure of the diffusion rate of adatoms at the surface, can be correlated directly to the calculated diffusion coefficient as per the Einstein-Smoluchowski equation[91]:

$$k_{diff} = 2 \ D_{eff} \ d^{-2}$$  \hspace{1cm} (9)

where $d$ is the internal lattice distance between metallic iron sites (2.8665 Å with a BCC structure)[92]. High $Da$ values translate into much higher electrochemical rates than the surface level diffusion rate, thus promoting the generation of irregular or dendritic structures. Figure 10 showcases the possible electrodeposition regimes, where the regions between dendritic, island and film morphologies has been indicated.
Figure 10. Theoretical surface morphology regimes as per the ratio of electrochemical rate \( A \) and self-diffusion rate \( k_d \). The three main mass diffusion control cases are represented: dendrite formation due to diffusion control (red), island formation due to mixed control (green) and film formation due to kinetic control (blue). The white box encases the experimental conditions used in this study.

Surface morphology is expected to distinctly change when one rate dominates over the other in two orders of magnitude[35]. The white dashed line encases the estimated region studied in this work, as per the values of \( P_2 \) and \( P_4 \) obtained via equations (3 – 7), compiled in Tables S1 – S6.

All three regions estimated in Figure 10 are formerly observed in the SEM micrographs of Figure 8. The most evident case of dendritic or diffusion controlled type of regime can be associated to deposition of iron with no additives, see Figure 8a, where extensive dendritic regions with some minor island areas still occur, which would entail a rate of electrochemical reaction just about two orders of magnitude greater than iron self-diffusion. Although this is feasible on the top left corner of the estimated FeED regime highlighted in Figure 10, we must note that assumption of \( A \approx k_e \) might be a slight oversimplification, as some of the dendrites appeared to already be detaching, meaning that the actual electrochemical rate would be higher.
thus pushing this electrodeposition regime further up into the dendrite formation zone. However, it must be noted that in iron electrodeposition systems, the distribution of these regimes and more specifically, the dendrite formation range is highly dependent on the composition of the electrolyte. Such dendrites have been reported to be a significant cell-performance defining factor not only in all-iron RFBs[34], and to a greater extent in numerous other systems that rely on electrolysis or electrodeposition of iron, such as electrowinning or surface finish technologies [37,93,94]

Full film-like type of deposition seems to only appear in electrolytes containing citrates or TBACl (see Figure 8c and 8f). The electrolytes containing these molecules therefore show the most balanced mass transfer and iron deposition rates, with predominantly smooth surfaces with minor protrusions evenly distributed. The smoothest surface, ascribed to the TABCl electrolyte, arises from the lowest experimental cell and plating currents (Figures S1 and 4), paired with slower mass transfer as we had hypothesized above due to the lateral diffusion of the bulky Fe-TBA* radical species[73], in the electrolyte and by the electrode surface, thus maintaining kinetic control as per the terms of equation 8. Similarly, the citrate electrolytes were characterized by a quick decomplexation step that allowed for increased nucleation and reduced HER rates (Figure 6a and Figure 7, respectively), while effectively managing the growth direction of the deposited layer, thus favoring an electrochemical reaction-dominated nucleation and growth regime when compared to the mass transfer of the iron adatoms. The remaining modified electrolytes, i.e., those containing borate, ascorbate and thiourea, generate structures that fall within a mixed control regime, or island-type electrodeposition. In the case of the borate additive, although we postulated previously that a decomplexation process is also taking place, as with citrates, this step occurs at a different rate, which generates bulkier, column-like protrusion on a relatively smooth surface, as seen in Figure 8b. As we advance towards regions where mass transfer and self-diffusion become of greater importance, we observe more noticeable island deposition. In electrodes coated with ascorbate electrolytes, we observe more distinct protrusions in the micrometric range, aided by the hydrolysis of Fe$^{3+}$. Additionally, the iron-ascorbate has been reported to form a more stable complex than the former[95], thus limiting the diffusion, release and self-diffusion rates of iron and therefore the system would fall under region more heavily influenced by mass transfer phenomena. Finally, electrolytes with thiourea produce the biggest protuberances, with large hemispherical structures 30-150 µm in diameter (Figure 8e) due to the
plating process taking place as segregated nucleation with seed growth, as stated above (see Figures 4e and 6e). In the SEM micrograph at high magnification (Figure 8e, bottom) we had observed a longitudinal flaky morphology due to the increased currents that accentuate concentration polarization effects at the electrode surface.

Therefore, we can conclude that estimating and controlling the resulting plated structures is crucial for safe, durable battery operation, especially towards the prevention of tridimensional or dendritic features, as these would promote ion depletion in the vicinity of the electrode. This preferential deposition can lead to limited electrolyte utilization in batteries, resulting in (partly) detached tridimensional structures, loosely packed coatings and limited capacity[87]. Under normal battery working conditions, it is expected that this 3D growth behavior will be exacerbated, as local current density can reach higher values than the limiting current density due to the geometry and uneven surface of current collector or ancillary structures, like porous transport media. This can lead to unusually high local overpotentials and severe dendrite formation. Therefore, electrodeposition is more likely to continue on these protrusions, increasing the expansion of tridimensional structures, which could pierce the membrane or separator of the cell, causing a short circuit and battery death[14,48]. The 3D growth of these structures is therefore directly linked to the effective ion diffusion rate on the proximity of the anode and the rate at which Fe²⁺ is consumed, and lowers the energy output and efficiency of the system. These dendrites are aggravated by self-acceleration arising from the formation of concentration gradients[96], as well as intrinsic lattice and surface energy properties of the metal iron during electrodeposition processes[97]. The dendritic protrusions are more likely to break and become detached, or “dead”, leading to irreversible capacity loss.

3.7. Influence on battery cycling and operation

The prior chronoamperometric analysis and the theoretical nucleation and HER kinetics analysis enables the comparison of the effects of the various electrolyte additives, gaining deeper understanding of the kinetics of the nucleation and competing HER process. Nevertheless, although we can provide general trends or estimations towards performance and efficiency of iron batteries, this single step deposition technique remains far removed from practical cell
operation. To bridge this operational gap, the long-term electrochemical performance of each
system was simulated by consecutive plating-stripping cycles in a symmetric Swagelok™ cell.
Results are depicted in Figure 11, which include the electrochemical impedance spectroscopy
and the subsequent voltage profiles of alternating charge-discharge cycles under galvanostatic
conditions.

The impedance spectra (Figure 11 a) show depressed semicircles in all cases, indicating an
overlap between mass and charge transfer processes[31]. This overlap could be attributed to the
coupled diffusive transport of active ions with the non-redox active chelates towards the
electrode surface. Such accumulation of species near the electrode surface could increase the
capacitive behavior, and overlay with the lower frequency response of diffusion of adsorbed
compounds prior to the electrodeposition step[98]. We also found that area-corrected ohmic
resistances were not highly dependent on the presence of additives (Figure S10). Borate-,
citrate- and thiourea-containing electrolytes display a significant reduction in the overall
impedance behavior, indicating a more facile redox response. This is in accordance with the
favored kinetics process due to the effects of the conjugated or π-type bonds[78], as seen in the
nucleation analysis, see Figure 6 above, and therefore with the increased battery cycling (Figure
11b). The impedance behavior of the ascorbate complex is observed to increase in both the real
and imaginary plane. This could be ascribed to the formation of oxides on the surface, as noted
in its crystallographic analysis (Figure 9d), reducing conductivity of the sample and hindering
access of ionic species to available reaction sites. The TBACl electrolyte data likewise displays
an increment in impedance, although more likely attributable to the somewhat sluggish transport
of the Fe-TBA* species and the curtailed density and rate of nuclei growth[74] (Figure 6f).
Therefore, unmodified acidic iron electrolytes display the lowest cyclability, with marked
instabilities in the voltage profile (Figure 11b). The dendritic structures seen in Figure 8a after a
single plating step would increase upon further cycling, accelerating the mismatch between the
crystallography and morphology between the electroplated layers, the rates of parasitic hydrogen
evolution and irreversible loss of capacity. Consequently and as we had anticipated, in cases
where such dendritic structures are prevented, there is a significant reduction in overvoltage
hysteresis in the case of the acid-based iron chelates, which reinforces the hypothesis of the
adsorption of these buffer complexes on the electrode surface, as previously reported in the
literature[85]. This is in agreement with their impedance profiles and increased faradaic efficiencies denoted in Figure 5.

Figure 11. Electrochemical data of the symmetric Fe$^{2+}$/Fe$^0$||Fe$^{2+}$/Fe$^0$ system with and without selected electrolytes: (a) Electrochemical impedance spectroscopy data and (b) temporal current-voltage profiles at 35.5 mA g$^{-1}$ and 0.6 C rate with ± 0.2 V cut-off voltages. Experimental data corresponds to the baseline electrolyte containing FeCl$_2$ 1 M and HCl 1 M (black), and modified electrolytes: electrolyte containing FeCl$_2$ 1 M and HCl 1 M and boric acid 100 mM (red), electrolyte containing FeCl$_2$ 1 M and HCl 1 M and citric acid 100 mM (blue), electrolyte containing FeCl$_2$ 1 M and HCl 1 M and ascorbic acid 100 mM (green), electrolyte containing FeCl$_2$ 1 M and HCl 1 M and thiourea 100 ppm (purple), and electrolyte containing FeCl$_2$ 1 M and HCl 1 M and TBACl 100 ppm (orange).

The capacity retention and stability for these improve with respect to the unmodified electrolyte, in the following order: Fe-citrate > Fe-borate > Fe-ascorbate, due to the combined effects of enhanced nucleation kinetics and superior crystallographic and structural properties, as seen in previous sections, such as denser and smoother deposits that are able to sustain more balanced
current density distributions upon subsequent plating and stripping. In the case of both organic additives, cycling behavior is similarly enhanced, although with certain limitations. Surprisingly, in the case of thiourea, despite the elevated partial plating current densities achieved and the strong improvements in impedance, cyclability is only moderately improved. Presumptively, this would be caused by the largely unrestrained HER side reaction, since this is not efficiently regulated in the operating potential range for this symmetric cycling study, as we reported above (Figure 7). Likewise, the electrolyte with TBACl also introduces an improvement in cyclability, albeit more moderate than the acid buffers. The TBACl electrolyte has consistently demonstrated inferior nucleation and growth kinetics, in addition to inferior mass transport properties throughout this work. Thus, despite its distinct ability to limit parasitic hydrogen generation, this additive concurrently interferes with the main iron plating process and overall battery cycling. Therefore, to achieve enhanced iron battery cycling (see Figure S18 battery cyclability with 75% capacity retention), we found that there needs to be a balance between, not only iron plating seeding and growth but also the stripping process, whose detailed mechanism is out of the scope of this work. More specifically, we found that highly stable iron complexes, such as borate- or citrate-based chelates render superior plating and overall symmetric cycling performance due to their balance between nucleation enhancement and epitaxial electrodeposition with HER suppression, simultaneously enabling significant reductions in mass and charge transfer resistances. We acknowledge that, despite the symmetric configuration being commonly used a in battery diagnostics[25,61], it may not fully represent the behavior of the full cell system, it can still provide valuable information as a proxy for cell degradation and lifetime limitations. Similarly, we believe that the findings and methodology established in this work can be extensible and help advance technologies that rely on iron or metal electrodeposition. Concrete examples of this are the high-purity iron layers required in the aerospace industry for safety purposes[99], electromagnetic properties such as magnetic shielding and memory in electronics and spintronics[100], ultrapurity of thin films for high-precision optical devices with controlled surface morphology and crystal orientation[101,102], medical implants[103] or in catalytic applications [104]

4. CONCLUSION
In this study, we employed a suite of electrochemical techniques, coupled with parameter fitting to physical models and crystallographic techniques to investigate and extract relevant metrics about the formation, growth and stripping of metallic iron for use in high power, aqueous all-iron RFBs. Using this systematic approach, we have gained fundamental insight into the poorly understood mechanism of nucleation and growth of iron electroplating. Our research investigates the plating kinetics and spatial distribution of the iron plating centers over a full range of potentials practical to iron-based battery operation, further corroborated by microscopic techniques and their effect on reaction specificity and faradaic efficiency. We hypothesize that for the studied system, the nucleation process does not follow the traditional progressive or instantaneous nucleation theories, but rather an intermediate case with a finite number of plating sites, with 3D diffusion dominated growth.

Furthermore, we explored the effect of pH on the kinetics of the process, and employed a number of acid chelates and other organic ligands with different moieties as a route to regulate the kinetics of iron electrodeposition and its distribution on the substrate. We propose that an adequate pH range for operation could be comprised between 0-0.5, despite the slightly more limited faradaic efficiencies, as there is the greatest balance between HER and electrodeposition kinetics, and quality of the resulting plated layers. Additionally we found that all additives studied in this work are able to tune the plating process, via changes in the mass transport properties of the species or preferential interactions with the iron anode, thus altering the density and placement of plating iron seeds, their nucleation and growth rate. Consequently, we successfully altered the final morphology and quality of the deposit. We found a trade-off between suppression of side reactions and non-uniform current density distribution with higher partial plating current densities. Additionally, we employed a symmetric Fe$^{2+}$|Fe(s) cell with stagnant electrolyte to carry out galvanostatic charge-discharge cycling as an experimental instrument to translate these fundamental findings into a workspace more representative of real RFB operation. We found that highly stable iron complexes, such as borate- or citrate-based chelates render superior plating and cycling performance. More specifically, considering the overall balance between nucleation enhancement and epitaxial electrodeposition with HER suppression, the citrate additive appears to be the most promising one as it simultaneously enabling significant increases in parameters such as nucleation rate or nucleation center density.
This in turn, showed reductions in mass and charge transfer resistances and increases in cyclability of ~50% compared to the non-modified electrolyte.

This study highlights the great potential to improve performance and selectivity by electrolyte engineering, which can allow the reaching of a deeper level of fundamental understanding regarding the interplay of redox species with other electrolyte components and the electrode surface, i.e. control over the ion-ion and solid-liquid interactions. These approaches of electrolyte engineering can be extensible to other electrochemical systems to increase selectivity or reversibility and therefore advance their widespread commercialization, such as other electroplating-stripping hybrid RFBs (e.g., Mg\textsuperscript{2+}|Mg, Ca\textsuperscript{2+}|Ca, Zn\textsuperscript{2+}|Zn, etc.). Similarly, additives can play a major role in well-established operations such as electrochemical water or solvent remediation, electrowinning or surface finishing processes, especially those relying on the formation of highly pure or morphologically controlled metallic thin films. For further efforts, we propose the exploration of concentration series or multi-additive formulations for greater optimization, or alternative electrode architectures, such as porous scaffolds with rational structures that enable higher capacity and rate performance.

**Supplementary Information**

Supplementary Information is available at the Elsevier Electronic Journals Library

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Conflict of Interest

The authors declare no conflict of interest.

Data availability

The data presented in this study can be provided by the corresponding author upon reasonable request.

Author Contributions

IGG. contributed to the conceptualization, methodology, validation, formal analysis, investigation, data curation, writing - original draft, writing - review and editing, and visualization. AFC. contributed to the conceptualization, funding, resources, writing - original draft, writing - review and editing, project administration, and supervision.

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Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AIB</td>
<td>All iron aqueous battery</td>
</tr>
<tr>
<td>CA</td>
<td>Chronoamperometry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>FeED</td>
<td>Iron electrodeposition reaction</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
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<tr>
<td>PFA</td>
<td>Perfluoroalkoxy</td>
</tr>
<tr>
<td>RFB</td>
<td>Redox flow battery</td>
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<tr>
<td>SEI</td>
<td>Solid electrolyte interface</td>
</tr>
<tr>
<td>SH</td>
<td>Scharifer and Hills nucleation model</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>

List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
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<tbody>
<tr>
<td>A</td>
<td>Nucleation rate for electrodeposited iron</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>Cb</td>
<td>Bulk concentration of Fe²⁺</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>Da</td>
<td>Damköhler number</td>
<td>-</td>
</tr>
<tr>
<td>D_eff</td>
<td>Calculated effective diffusivity of Fe²⁺</td>
<td>m² s⁻¹</td>
</tr>
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$d$</td>
<td>Internal lattice distance between metallic iron sites</td>
<td>m</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard redox potential</td>
<td>V</td>
</tr>
<tr>
<td>$F$</td>
<td>Faradaic constant, 96485 C mol$^{-1}$</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density</td>
<td>mA cm$^{-2}$</td>
</tr>
<tr>
<td>$i_{\text{max}}$</td>
<td>Maxtum current density</td>
<td>mA cm$^{-2}$</td>
</tr>
<tr>
<td>$k_e$</td>
<td>Electrochemical reaction rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{diff}}$</td>
<td>Surface diffusion rate</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$MW$</td>
<td>Molecular mass of iron</td>
<td>kg mol$^{-1}$</td>
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<tr>
<td>$N_0$</td>
<td>Superficial density for iron electrodeposition on the substrate</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>$t_{\text{max}}$</td>
<td>Nuclei diffusion boundary layer overlap time</td>
<td>s</td>
</tr>
<tr>
<td>$t_{\text{nuc}}$</td>
<td>Onset time for metal nucleation</td>
<td>s</td>
</tr>
<tr>
<td>$z_{\text{HER}F}$</td>
<td>Molar charge exchanged during hydrogen evolution reaction</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$z_{\text{FeED}F}$</td>
<td>Molar charge exchanged during iron electrodeposition reaction</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of the metallic deposit</td>
<td>kg m$^{-3}$</td>
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**Greek**

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