Electrodeposition experiments in microgravity conditions

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Abstract. Metal electrodeposition may produce irregular deposits with various morphologies. For liquid electrolytes a precise study of these deposits may be complicated by convective motion due to buoyancy. Zero-gravity (0g) conditions provided by parabolic flights give a straightforward mean to avoid this effect: we present here 0g electrodeposition experiments, that we compare to ground experiments (1g).

Two electrochemical systems were studied by laser interferometry, allowing to measure concentration variations in the electrolyte: copper deposition from copper sulfate aqueous solution and lithium deposition from an ionic liquid containing LiTFSI. For copper, concentration variations were in good agreement with theory. For lithium, an induction time was observed for the concentration evolution at 1g: due to this induction time and to the low diffusion coefficient in the ionic liquid, concentration variations were hardly measurable in the parabolic flight 0g periods of 20 seconds.

1. Introduction
It has been known for decades that metal electrodeposition in the absence of a supporting electrolyte may produce irregular deposits with various morphologies. This phenomenon has attracted much interest in the last 50 years. From the viewpoint of fundamental electrochemistry, dendritic electrodeposits may provide simple model systems to study Diffusion Limited Aggregation (DLA) phenomena [1]. On the other hand, dendritic growth was also intensively studied for practical reasons, in particular because of its detrimental role in battery technology [2]. This phenomenon has limited the use of all-solid-state lithium batteries with metallic lithium negative electrodes: although one of the most promising technologies to meet the requirements of electric power sources in novel applications (portable electronic devices or electric vehicles), this technology is not yet available because dendritic growth may appear during battery charging. Hence, controlling the morphology of the metal deposited on a lithium metal electrode is still an important issue in order to avoid dendritic growth in lithium batteries.

However, for liquid electrolytes, and whatever the electrochemical system under concern, a precise study of dendritic growth mechanisms may be complicated by convective motion due to buoyancy [3]: even in thin, quasi-two-dimensional horizontal cells with vertical electrodes, electrodeposition is accompanied by a gravity-induced fluid flow at the electrodes (figure 1). This
effect is due to the electrolyte density decrease at the cathode (due to the concentration decrease) or increase at the anode (concentration increase): it has been extensively studied in the recent literature, both theoretically [4-6] and experimentally [7-12]. Convective motion mixes the electrolyte and tends to homogenise the concentration. The effect depends on cell configuration, salt concentration, and current density [4]. This convection driven by buoyancy was shown to increase the instability of the system [12].

![Figure 1](image.png)

**Figure 1.** Schematic view of an electrochemical cell in the vicinity of vertical electrodes: a convective motion is induced in these regions, due to the electrolyte density decrease at the cathode (concentration decrease) or increase at the anode (concentration increase).

Obviously, zero-gravity experiments [13] should give a straightforward mean to avoid this effect: apart from gravity, no other parameter is altered. However, these experiments are relatively difficult to work out and of short duration (around 5 - 25 s in the most affordable facilities: drop tower and parabolic flight).

Hence, several other methods have been proposed to minimise the convection driven by buoyancy:
- very thin cells (cell thickness less than 30 μm) and/or electrolytes with very low concentration, below 0.01 mol L\(^{-1}\) [9]. However in practical cases, electrolyte concentrations are much higher than this limit: for example, electrolytes with concentration over 1.0 mol L\(^{-1}\) are used in Li batteries. The limited concentration range mentioned above thus restricts the interest of this method.
- gel [7], or electrolytes with increased viscosity [14] allowed for measurements without the above limitation. However, the chemistry involved in these electrolytes may be markedly different from that involved in the absence of additives.
- several authors [7, 9, 12, 15-18] used thin cells in a vertical position, with a plane cathode set horizontally on top of the cell, and facing downward. It is called “cathode over anode” (C/A) type cell. For example, Marshall et al. [12] showed that this configuration enables to obtain a stable regime. Using this method, Morisue et al. could evidence the gravitational effect on nucleation phenomena in copper electrodeposition onto a TiN substrate [19]. González et al. could measure impedance diagrams of the electrolytic cell at the onset of dendritic growth [18].

These experiments, with a cathode set horizontally on top of the cell, are easy to handle, and they have no time limitation. However, obviously gravity is still present, and convective motion may appear, in particular when the current density distribution (hence the concentration distribution) is not uniform along the electrodes, because the electrodeposits increase the surface roughness.

In conclusion, zero-gravity experiments may appear as a unique way for avoiding the convective motion driven by buoyancy in electrodeposition in conditions well controlled and free from any of the above mentioned parasitic effects.

Previous studies have shown that even short zero-gravity experiments may provide interesting information on the preliminary stages of dendritic growth in electrodeposition. In particular, Fukunaka et al. performed copper electrodeposition experiments from CuSO\(_4\) aqueous solution [13]. The experiments were carried out in a drop shaft allowing free falls for more than 8 seconds under zero-gravity environment. Ionic concentration profile in the electrolyte was measured by interferometry: the diffusion layer thickness was shown to increase linearly with the square root of time, in good
agreement with theoretical calculation. Due to natural convection, the diffusion layer thickness was shown to increase much faster at 1g than at 0g. Also, at 0g, the deposit consisted in fewer, larger grains than at 1g.

We present in this paper a study of electrodeposition in the zero-gravity environment provided by parabolic flights. This project was supported by the Centre National d'Etudes Spatiales (CNES): it planed copper electrodeposition experiments on copper electrode and lithium electrodeposition on Ni electrodes in the Airbus A300 from Novespace. During these flights, almost zero-gravity conditions were available over 20 to 25 seconds. The project included concentration measurements by laser interferometry, and similar but longer experiments performed at 1g in the cathode over anode configuration. Both series of experimental results were to be compared with numerical calculations.

2. Experimental

The project presented here consisted in carrying out electrochemical experiments during zero-g periods provided by parabolic flights. Although limited, the duration of these experiments indeed allowed to explore ranges of parameters hitherto inaccessible. They were supplemented by experiments in cells whose geometry (C/A cell) allowed longer experiments, while minimizing the effect of concentration gradients.

The experiments were carried out in a pseudo 2 D-cell (figure 2). Care was taken to obtain a well defined cell geometry: see Ref. [20] for details. Copper electrodes were used for the copper electrodeposition and nickel electrodes were used for lithium electrodeposition: they were held between two glass plates enabling to observe in situ the electrolyte (figure 2).

![Figure 2. Schematic view of the cell](image)

The active part of the cell had a parallelepiped shape, with dimensions L, the active length of the electrodes, l, the inter-electrode distance, and d, the thickness of the electrodes, respectively. Practical values were: L = 0.8-1.5 cm, l ≈ 0.09 - 0.3 cm, d ≈ 0.012 - 0.1 cm. The lateral faces of the electrodes were coated with a hydrophobic film which limited the invasion of the electrolyte in between the electrodes and the glass plates. After filling the cell with the electrolyte, we sealed it with a two-component resin before taking off: this allowed to keep it under almost constant conditions for several hours [20]. During the flight, the temperature in the plane was 18°C. Two electrochemical systems were studied: copper deposition from 0.1 and 0.2 mol L⁻¹ aqueous CuSO₄ solutions and lithium deposition from an ionic liquid. The ionic liquid was N-methoxymethyl-N-methylpyrrolidinium bis(trifluoro-methane-sulfonyl)imide containing 1.0 mol L⁻¹ LiTFSI.

In these microgravity experiments, a concentration variation of the electrolyte induced a variation of the refractive index which was measured by a common path laser interferometer.

Laser interferometry is a well known technique for measuring the concentration changes in electrochemical processes [21-25]. In this study, we used the interferometer described in Ref. [13] to measure in situ the variation of the ionic concentration in the electrolyte between cathode and anode. This interferometer, provided by Olympus, was designed for 0g experiments. Because we used thin cells (0.1 or 1 mm), we expected light deflection due to refractive index gradients [26] to be
negligible. The laser source was a laser diode with 685 nm wavelength. The change in the refractive index was given by

\[ d \Delta n = S \lambda \]  

(1)

where \( d \) is the optical path length in the electrochemical cell (here the electrode thickness), \( \Delta n \) is the change of refractive index, \( S \) is the shift of interference fringes, and \( \lambda \) is the laser wavelength. The relationship between refractive index and concentration is given by:

\[ \Delta n = \left( \frac{\partial n}{\partial C} \right) \Delta C \]  

(2)

In the case of copper in a CuSO\(_4\) aqueous solution, we used \( \left( \frac{\partial n}{\partial C} \right) = 0.0279 \). This value was obtained at 23°C [24]. We kept the same value at 18°C, because the temperature coefficient of the refractive index of water is approximately \( 10^{-4}/\degree C \) at this temperature [27]. In the case of lithium in the liquid ionic, \( \left( \frac{\partial n}{\partial C} \right) = 0.005 \) [28] was taken. Using equations (1) and (2), the change of concentration could be determined from the measurement of the shift of the interference fringes. The evolution of this shift was recorded by means of a CCD camera. An experiment thus consisted in applying a constant current or a constant potential to the electrochemical cell, while capturing a series of pictures showing the evolution of the interference fringes.

In the ground experiments a Mach Zehnder interferometer was used [29], with a laser diode with 638 nm wavelength.

3. Results

3.1. Copper deposits

We have reported elsewhere [7, 11, 29] concentration measurements obtained in 1g conditions, both for vertical electrodes, and for horizontal electrodes in the C/A configuration. In the latter case, concentration profiles observed before the onset of dendritic growth were in good agreement with calculations neglecting the presence of gravity [7, 29]. On the other hand, in experiments performed in cells with vertical electrodes concentration profiles were markedly different, due to the presence of buoyancy induced convection [7-11].

We present here concentration measurements in the electrolyte at 0g. Figure 3 shows an example of interference fringes recorded during one parabola, before and 15 seconds after the beginning of cell polarization. The fringes are bent in the vicinity of the cathode, at the bottom of the figure, because of the variation of concentration.

![Figure 3](image-url)

**Figure 3.** Interference fringes recorded before and 15 s after the onset of Cu deposition. The fringes are bent in the vicinity of the cathode (bottom of the figure) because of the concentration variation. The shift to the right hand side corresponds to a decrease of the refractive index, hence of the concentration. Electrolyte concentration is 0.1 mol L\(^{-1}\), current density is 8 mA cm\(^{-2}\). Cell thickness is 0.1 cm.
This can also be seen in figure 4, showing the position of the interference fringes as a function of position at three different times.

![Figure 4](image)

**Figure 4.** Shift of the interference fringes as a function of the distance to the cathode at three different times after the onset of Cu deposition. Same conditions as in figure 3.

These concentration variations were also numerically calculated, using general equations describing transport phenomena in electrochemical systems [31], and taking into account the variation of the diffusion coefficients with concentration in CuSO$_4$ aqueous solution [32]. A detailed presentation of the application of these equations to the Cu/CuSO$_4$ system is given in Ref. [7].

Variation of the surface concentration at the cathode as a function of time during and after one parabola is shown in figure 5, and compared with theory. As shown in figure 5, we found a good agreement between experimental and theoretical results, thus confirming 1g results for the C/A cell. After the end of the parabola, the concentration at the cathode rapidly returned to its initial value (figure 5): this was due to the large gravitational level (~ 1.5g) imposed at this time in order to drive back the plane to its normal flying conditions.

Our experiments did not enable us to observe dendritic growth of copper in 0g conditions, because the dendrites only appear after an induction time $t_s$, the so-called Sand time [30]. Sand time varies as

$$t_s = \frac{\pi e^2 D (1 + \mu_c/\mu_a) C_0^2}{J^2}$$

where $e$ is the electronic charge, $D$ the diffusion constant, $\mu_c$ and $\mu_a$ the cationic and anionic mobilities respectively, $C_0$ is the initial ionic concentration and $J$ the current density.

To obtain a Sand time shorter than 10 seconds for example, would require a high current density (larger than 20 mA cm$^{-2}$) and still, the time available for observing dendritic growth would be very short. Experimental environment did not provide such conditions in this parabolic flight campaign. Further experiments are thus necessary to explore dendritic growth itself.
3.2. Lithium deposits

As mentioned earlier, a series of experiments were performed at 1g. A typical result is given in figure 6, showing the variation of the cathode surface concentration as a function of the square root of time. In this experiment, the applied current density was 1 mA cm\(^{-2}\) and cell thickness was \(d = 0.1\) cm. One clearly sees a first stage, where the concentration variation is very small. Then, after 90 s, the variation is much more rapid. Such an induction time was already reported [17]. In the present case, the observed induction time might be due to side reactions of the electrodeposited lithium metal.

The diffusion coefficients in ionic liquids are very low. From the variation of the diffusion layer thickness in the experiment illustrated in figure 6, we estimated the following value for the diffusion coefficient: \(D \sim 10^{-7}\) cm\(^2\) s\(^{-1}\). This value is in good agreement with that measured by other methods [33]. The concentration variations are compared in figure 6 with theoretical values [31], which are calculated without taking into account the concentration dependence of the diffusion coefficient. The result obtained taking into account the above value of \(D\) and a transport number of 0.35 for Li\(^+\) ion is shown as a straight continuous line.

At 0g, we could not observe any variation of the concentration profiles in the electrolyte. Due to the very low diffusion coefficient and to the induction time mentioned above, the concentration variations due to Li deposition during the first 20 seconds were very small, and the concentration boundary layer thickness was at most 10 \(\mu\)m: thus concentration variations were hardly detectable by our interferometer. The Li deposition experiment would thus require longer zero-g times.

Figure 5. Variation of ionic concentration in copper sulfate at cathode during one parabola: experimental results (closed circles), calculated results (dashed line). The variation of \(g/g_0\) is shown as a continuous line. The horizontal line shows the initial concentration, the two vertical lines show the beginning and the end of the cell polarization. Same conditions as in figure 3.
Figure 6. Deposition of lithium from ionic liquid: variation of cathode surface concentration as a function of the square root of time after the onset of polarization: experimental results (filled circles), calculated results (straight continuous line). Current density is 1 mA cm\(^{-2}\). Cell thickness is 0.1 cm.

4. Conclusion
We could perform electrodeposition experiments in the microgravity conditions provided by the parabolic flight facility operated by Novespace. The evolution of concentration profiles measured in the electrolyte by laser interferometry was consistent with theory and with previous experiments performed at 1g for cells in the C/A configuration. However, because of their limited duration, parabolic flight experiments could only provide results on the early stage of electrodeposition. A more complete study would require further zero-g experiments: for studying dendritic growth of copper, or for deposition of lithium from ionic liquids, longer times would be necessary (such as those available in sound rockets or in the International Space Station). Such study should give access to experimental conditions different from those available on ground, even in the C/A configuration, in particular in the case where the current density distribution (hence the concentration distribution) is not uniform along the electrodes. These improvements are considered in the framework of a project developed by an “Electrochemical Nucleation & Growth” ESA Topical Team.

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