

# Onset of dendritic growth in lithium/polymer cells

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## Abstract

We have studied the onset of dendritic growth in symmetrical lithium/polymer/lithium cells, at current densities ranging from  $2 \times 10^{-2}$  to  $3 \times 10^{-1}$  mA cm<sup>-2</sup>. We observe that dendritic growth starts at a time  $t_{cc}$  which follows a power law as a function of the current density, very close to Sand's law. However, in our experimental conditions no Sand behavior is expected. We attribute this surprising result to the existence and/or formation of local inhomogeneities on the surface of the electrodes. We discuss a preliminary model accounting for the observed behavior. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Dendritic growth; Lithium/polymer/lithium cells; Sand's law

## 1. Introduction

Lithium/polymer batteries are among the most promising electrical energy storage systems. In particular, metallic lithium is a good candidate for the anode, since it has a very high theoretical specific capacity. However, the formation of dendrites affects the charge efficiency of this type of electrode, even in a polymer electrolyte where this phenomenon is supposed to be limited [1]. Our aim was to understand the dendritic growth mechanisms in order to prevent this undesirable effect. In particular, the onset of the growth is an important issue, because, once they have started, the dendrites usually grow across the electrolyte and eventually short-circuit the battery.

In previous publications [2–4], we showed that, in a range of experimental conditions, dendritic growth occurs according to the model proposed by Chazalviel [5]. When polarizing a cell with a binary electrolyte, the ionic concentrations in the vicinity of the negative electrode drop to zero at Sand's time  $\tau_S$  [6]: according to Chazalviel, a different behavior then occurs for the anionic and for the cationic concentrations, leading to an excess of positive charges at the negative electrode. This results in a local space charge associated

with a large electric field. This situation induces instabilities such as dendritic growth [5]. The model then predicts that dendrites appear at a time very close to Sand's time. It also predicts that the dendrites grow at a velocity  $v = -\mu_a E$  ( $\mu_a$  is the anionic mobility,  $E$  the electric field), which is the drift velocity of the anions in the field  $E$ . This was confirmed experimentally [2,3].

However, we also showed that, when the current density is low, the above model cannot, in principle, explain the observed dendritic growth, because no Sand behavior is expected in these conditions. On the opposite, a steady state is expected, where the concentration variation should be small [3,4].

In this paper, we present a detailed study of the onset of dendritic growth in symmetrical lithium/polymer/lithium cells under galvanostatic conditions, at low current densities. We also propose a model to explain this growth. This model predicts a destabilization of the concentration distribution in the electrolyte, due to the specific properties of the Li/electrolyte system. This destabilization leads to large variations of the concentration in the direction parallel to the electrodes: eventually depleted zones appear near the negative electrode, which may create a situation close to the conditions of Chazalviel's model.

## 2. Experimental conditions

The polymer electrolyte consisted of poly(ethylene oxide) (MW =  $3 \times 10^5$ ). The lithium salt was LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>

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(abbreviated in LiTFSI), discovered by Armand et al. [7,8]. The salt concentration in terms of O/Li ratio was in the range 20–30. Preparation details were given elsewhere [9].

In most experiments, we used cells having a geometry close to the geometry of actual batteries: in this case, the cells essentially consisted of two lithium foils sandwiching a polymer electrolyte layer about 50–100  $\mu\text{m}$  thick. In specific cases, we used cells permitting in situ optical observation of the electrolyte [2–4,9].

For both kinds of experiments, the cell was put in a furnace and heated at 70–100°C (at 80°C, we measured a conductivity of  $9.1 \times 10^{-4} \text{ S cm}^{-1}$  for the electrolyte). The cells were polarized under galvanostatic conditions, with current densities in the range 0.02–0.3  $\text{mA cm}^{-2}$ .

### 3. Experimental results

In the current density range that we have investigated, previous in situ studies [3,4] showed that the dendrites had needle-like morphologies: they appeared as bright, metallic filaments. Their cross-section was about 10–20  $\mu\text{m}$  which made them very fragile.

In Fig. 1 we show a typical time variation of the cell voltage measured at a current density  $J = 0.05 \text{ mA cm}^{-2}$ . After a rapid increase of the voltage (step 1 in Fig. 1), one observes a quasi-stationary behavior for about 43 h (step 2). Then a sudden decrease is observed (see the arrow in Fig. 1, step 3), which is attributed to a partial short-circuit of the cell by a dendrite. A rapid degradation of the cell follows (step 4).

The initial increase of the voltage and the following stationary behavior correspond to the formation of a steady state, as expected in these experimental conditions. Indeed, at low current density, diffusion efficiently smoothes the concentration profile: if we consider our cell as a parallelepiped, with parallel electrodes facing each other, the

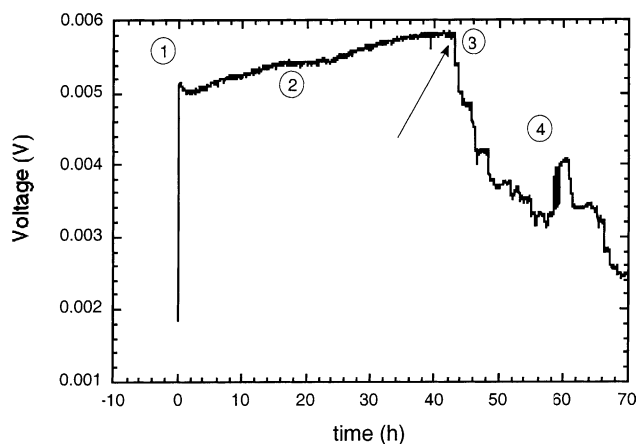


Fig. 1. Time evolution of the cell voltage ( $J = 0.05 \text{ mA cm}^{-2}$ , see text). The arrow shows a sudden decrease of the voltage, occurring when a dendrite partially short-circuits the cell.

system tends to a steady state where the concentration linearly increases from  $C_0 - \delta C^-$  at the negative electrode to  $C_0 + \delta C^+$  at the positive electrode ( $C_0$  is the initial concentration). Assuming an homogeneous ionic distribution in the directions parallel to the electrodes, and no space charge, one can easily show [3,4] that,  $\delta C^- \sim \delta C^+ \sim \delta C = (\mu_a/(\mu_a + \mu_c))JL/2eD$  (where  $\mu_a$  and  $\mu_c$  are the anionic and the cationic mobilities,  $L$  the inter-electrode distance,  $J$  the current density,  $e$  the electronic charge,  $D$  the ambipolar diffusion constant).

Depending on the cell, the sudden decrease which is observed on  $V(t)$  may be either followed by a temporary return to the previous stationary value, or by a further decrease of the voltage. In all cases the voltage never goes to zero: we attribute this behavior to the non-zero resistance of the dendrites. Optical absorption reveals that the sudden decrease of  $V(t)$  occurs approximately at the time when the dendrite has entirely crossed the inter-electrode space.

In fact, we observe that partially grown dendrites have very little, or no effect on the voltage. This is due to their relatively high resistance (that we estimate to be of the order of 10–100  $\Omega$  for a length of 100  $\mu\text{m}$ ). Hence, as long as the dendrite does not completely short-circuit the cell, the overall impedance of the cell is only very slightly modified. For the same reason, even a complete short-circuit will only partially decrease the voltage.

In Fig. 2 we show the time  $t_{cc}$  at which the voltage jump is observed, as a function of the current density  $J$ . Surprisingly, the time  $t_{cc}$  follows a power law as a function of  $J$ , very close to Sand's law [6]:

$$t_{cc} \sim \tau_S = \pi D \left( \frac{eC_0}{2J} \right)^2 \left( \frac{\mu_a + \mu_c}{\mu_a} \right)^2 \quad (1)$$

However, in Sand's theory, the transverse ionic concentration gradient is determined by the current density, and at the current densities shown in Fig. 2, the concentration is not expected to decrease to zero.

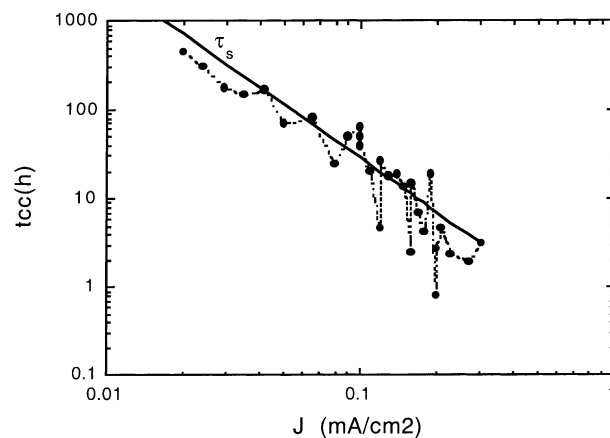


Fig. 2. Variation of the short-circuit time  $t_{cc}$ , as a function of the current density at 90°C. The solid line shows Sand's time  $\tau_S$ , with a  $J^{-2}$  dependence.

Furthermore, the optical experiments reveal that the dendrites grow at the velocity predicted by the Chazalviel model,  $v = -\mu_a E$ . For TFSI  $\mu_a$  is expected to be of the order of  $3 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . For a current density of  $0.05 \text{ mA cm}^{-2}$ , this results in a velocity of  $5 \times 10^{-3} \text{ } \mu\text{m s}^{-1}$ .  $\mu\text{m}$  cell in approximately 20,000 s, a time one order of magnitude smaller than the observed  $t_{cc}$ . At lower current densities, this difference will be even larger, as the time  $t_{cc}$  increases as  $J^{-2}$ , whereas the time needed to cross the cell increases as  $J^{-1}$ . In fact, for all current densities that we have investigated,  $t_{cc}$  is very close to the time at which the dendrites start growing.

Moreover, experiments performed at various temperatures in the range 70–100°C show that the time  $t_{cc}$  increases almost proportionally to the diffusion constant of the ionic species. This again is in agreement with Sand's behavior. In principle it should be interesting to observe the dependence of  $t_{cc}$  on the concentration  $C_0$ , as the Sand time is expected to vary as  $C_0^2$ . However, changing the concentration also changes the conductivity of the cell, the diffusion constant and the transport numbers. As we could not change the concentration on a wide range, this experiment did not provide a clear verification of the expected behavior.

We attribute the surprising result presented above, i.e.  $t_{cc} \sim \tau_S$ , to the existence and/or formation of local inhomogeneities at the surface of the electrodes (related either to the geometry of the electrode or to the passivation layer). Due to these inhomogeneities, the concentration distribution tends to become strongly non-uniform. The characteristic time for the onset of this non-uniformity is limited by diffusion, and depends on the inhomogeneities of the current density. We present in the next section a preliminary model describing this effect. The main result is that it predicts a Sand-like dependence very close to the observed behavior.

#### 4. Destabilization of the concentration distribution

We know that the passivation layer at the Li/electrolyte interface is very non-uniform. These non-uniformities (both in the geometry and/or in the composition of the layer) may probably occur at very different scales (from much below  $1 \text{ } \mu\text{m}$  to cms). Another characteristic feature of our cells is that the inter-electrode distance  $L$  is several orders of magnitude smaller than the dimension  $L_{\parallel}$  of the electrodes in the other directions.

We propose the following explanation for the behavior we have described above. Due to the non-homogeneities in the electrode surface resistivity, we can expect fluctuations in the current density, with a characteristic length of the order of the passivation layer thickness. Locally, since the inter-electrode spacing is small, the current density fixes the concentration gradient. However, the current density is not fixed locally, which may induce large concentration changes in the directions parallel to the electrodes. Hence, even for small values of the current density, depleted zones

may appear in various regions of the cell, as soon as the correlation length of the inhomogeneities is large enough. Furthermore, since the limiting mechanism for depletion is still diffusion, we recover a law similar to Sand's law for the apparition of the instabilities. Now, this transverse Sand's time is of the order of  $e^2 DC_0^2 / (\delta J)^2$ : the amplitude  $\delta J$  of the current density fluctuations may be of the order of the applied current density  $J$  in the case of lithium. This could explain why  $t_{cc} \sim \tau_S$ .

Hence, the behavior that we describe can be viewed as a Sand behavior in the direction parallel to the electrodes. Preliminary numerical calculations confirm that, provided that the above hypotheses are fulfilled (large  $\delta J$ ,  $L_{\parallel} \gg L$ ), we obtain this modified Sand behavior. We are now working on a more precise formulation of our model [10].

Moreover, we observed the onset of concentration instabilities in electrochemical deposition of Cu from  $\text{CuSO}_4$  in water, in cells where the inter-electrode distance was small compared to the length of the electrodes [11]. However, the properties of the Cu/ $\text{CuSO}_4$  interface are very different from those of the Li/polymer interface, and the results cannot be directly compared. A direct measurement of the concentration in Li/PEO cells is presently underway.

#### 5. Conclusion

Systematic measurements on symmetric Li/PEO cells reveal that dendritic growth starts after a time  $t_{cc}$  very close to Sand's time  $\tau_S$ . This is very surprising because in the range of current densities we investigate, no Sand behavior is expected. To explain this apparent contradiction we propose a model predicting a destabilization of the concentration distribution in directions parallel to the electrodes. Due to these instabilities, a modified Sand behavior is obtained, which explains the observed variation of  $t_{cc}$  with temperature and current density. We are now working on a generalization of the above ideas to real batteries.

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