

Theoretical pulse charge for the optimal inhibition of growing dendrites

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ABSTRACT

Dendritic growth during charging period is one of the main barriers for the rechargeability of conventional batteries. Additionally this phenomenon hinders the utilization of high energy density metal candidates by limiting the safety and allowable operating condition for these devices. We address the role of square wave pulse on the growth dynamics of dendrites in the continuum scale and large time periods by formulating an analytical criterion. Our dimension-free analysis permits the application our results to a variety of electrochemical systems in diverse scales.

INTRODUCTION:

Rechargeability has been one of the main challenges of conventional batteries, which directly affects their stability, safety and amount of utilized material. One of the main barriers for the reversible electrodeposition is the formation of highly porous whiskers, called dendrites. [1] Although the graphite electrode in the lithium ion battery has a considerable porosity, these microstructures still grow on its surface significantly. The amount and rate of growth exacerbates when replaced with alternative high-energy metals, with packed-structure. In particular lithium metal is arguably one of the most promising anode candidate materials for use in high-energy and high-power density rechargeable batteries. [2] Possessing the lowest density and smallest ionic radius, lithium has a very high gravimetric energy density ($\rho = 0.53 \text{ g.cm}^{-3}$). Furthermore

lithium is the most electropositive metal ($E^0 = -3.04$ vs SHE), therefore coupling with any other cathode compound, it will likely provide the highest possible voltage, making it suitable for high-power applications such as electric vehicles.[3] The prominent issue with the lithium comes from its very low surface energy, leading to the formation of thermodynamically favorable branched dendrites during electrodeposition during and after each charge period. [4] The accelerating amorphous structures can occupy a large volume in the cell, possibly could reach the cathode and short the cell. Dendrites can also detach from their thinner necks through electrodisolution during subsequent discharge period. Researchers have investigated how dendrites growth depends on such factors as current density,[5] electrode surface morphology[6, 7] and impurities [8, 9], solvent and electrolyte chemical composition [10, 11], electrolyte concentration [12], powder electrodes [13], temperature [14, 15] and mechanics [16]. Recent conventional characterization techniques also include NMR [17] and MRI. [18]

Pulse method has previously been utilized for uniform electroplating. [19, 20] Earlier, we found experimentally that the optimum rest period is related to the relaxation of double layer in the blocking electrode system [21] which can be expressed as RC time. [22] We explained qualitatively how relatively longer pulse periods with identical duty cycles (or idle ratio) will lead to longer quickening dendrites. We developed coarse grained computationally affordable algorithm that allowed us to reach to the experimental time scale (ms), which provided insights for current study. In this paper, we continue by developing dimension-free analytical criteria for optimizing the optimal pulse charging parameters.

METHODOLOGY:

The dendrite growth process can typically be divided by two stages of *initiation* and *propagation* which occur in series. The former occurs due to initial defects [23] and asperities in the surface [24, 25] and the latter occurs due to Brownian motion. Our focus in this paper is on tuning the parameters for this stage. In general, pulse charging in its simplest form consists of trains of square pulse wave (t_{ON}) and square rest (t_{OFF}) period of current (or voltage) (Figure 1a). Therefore, it can uniquely be defined with two parameters. The idle-ratio (γ) determines how is the proportion of rest-to-charge period as:

$$\gamma = \frac{t_{OFF}}{t_{ON}} \quad (1)$$

while the pulse frequency (f) controls the repetition rate of pulse waves:

$$f = \frac{1}{t_{ON}} \quad (2)$$

We should emphasize that the constraint for the pulse charging is the amount of charge; therefore if value of idle ratio increases, the time for the same amount of charge gets extended. In general the electrochemical flux is generated from the gradients of concentration (∇C) and electric potential ($\nabla \phi$). At the atomic scale, the ions of higher concentration regions tend to collide more and, given enough time, they diffuse to lower concentration regions following Brownian dynamics. In the continuum scale and time intervals larger than in inter-collision time scales (fs), these random movements lead to the diffusive displacement $\delta \vec{r}_D$ of an individual ion that can be described by the diffusion length as: [26]

$$\delta \vec{r}_D = \sqrt{2D^+ \delta t} \hat{g} \quad (3)$$

where D^+ is the cationic diffusion coefficient in the electrolyte, δt is a significantly large time intervals than inter-ionic collisions and \hat{g} is a normalized random vector in space, representing Brownian dynamics.

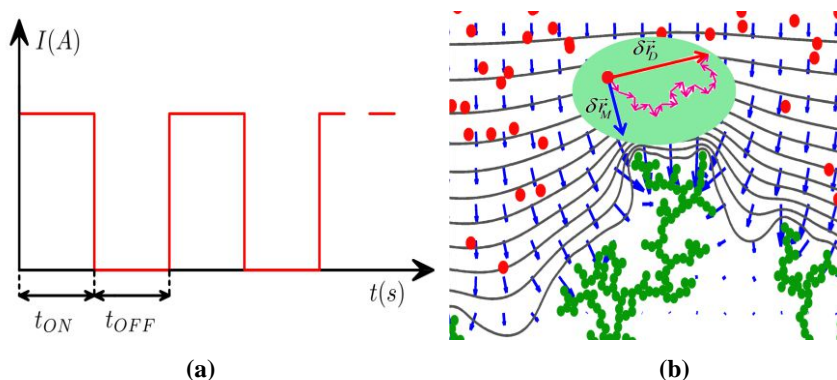


Figure 1: (a) Square pulse-wave with representative parameters. (b) Schematics of displacements in the coarse-grained model.

Given sufficient period of time, the multidirectional random vector \hat{g} will cause the uniformization of ions in space and will abolish the existing concentration gradients. The diffusion length represents the average progress of a diffusive wave in time, which is obtained from diffusion equation. [27]. On the other hand, within the same amount of time δt , the ions tend to acquire drift velocity in the electrolyte medium, and their electromigrative displacement $\delta \vec{r}_M$ is given as:

$$\delta \vec{r}_M = \mu^+ \vec{E} \delta t \quad (4)$$

where μ^+ is the mobility of cations in electrolyte and \vec{E} is the local electric field. Mobility is related to diffusivity by Einstein relation ($D^+ = \mu^+ k_B T$) and electric field is gradient of electric potential ($E = \nabla \phi$). Therefore the total effective displacement $\delta \vec{r}$ with neglecting convection (Rayleigh number $Ra < 1500$) would be:

$$\delta \vec{r} = \delta \vec{r}_D + \delta \vec{r}_M \quad (5)$$

The vector sum indicates the importance of direction in equation 4. The diffusion either can help the migration or can hurt it based on the direction of the local gradients of concentration and electric potential. Figure 1b illustrates the corresponding displacement vectors in relatively longer time periods that inter-ionic collisions. While electromigrative displacement is toward electric field, the diffusive displacement is in random direction (due to vector \hat{g}) and tends to even out the existing concentration gradients. The ionic flux is the result of cumulative contribution from diffusion and electromigration. During pulse period both mechanisms are responsible for ionic flux, while the diffusion is the sole drive during the subsequent idle period for the relaxation. Therefore we base our formulation on their interplay. Obviously, the diffusion length scales as $\sim t^{1/2}$ and electromigration scales with t ; Therefore comparing linear and square root trends, one expects that after giving a sufficient time δt_{eq} the mean distance that the ion moves due to the electric field gets larger than the mean distance of its random walk; the comparison of equations (3) and (4) leads to:

$$\delta t_{eq} = \frac{2RT}{\mu^+ E^2} \quad (6)$$

The diffusion displacement is a random walk, therefore it can either contribute to electromigration or prevents its progress (Figure 1b), therefore for a given period of time (δt), we have:

$$\left| \mu^+ \vec{E} \delta t \right| - \left| \sqrt{2D^+ \delta t} \right| \leq |\delta r| \leq \left| \mu^+ \vec{E} \delta t \right| + \left| \sqrt{2D^+ \delta t} \right| \quad (7)$$

where μ^+ , \vec{E} and D^+ are the local cations mobility, electric field and diffusivity respectively. During each idle period, the concentrated ions in the dendritic tips tend to diffuse away. Therefore in order for destroy the concentration gradient created in the tip of dendrites during the charge, the average displacement during idle period has to be competitive enough. The comparison from equation 7 leads to:

$$\gamma > \left(1 + \sqrt{\frac{\mu |E|^2 t_{ON}}{2RT}} \right)^2 \quad (8)$$

RESULTS AND DISCUSSIONS:

Equation (8) in fact represents the region where the possible solution lies with $\delta t \in [0, \delta t_{eq}]$. This represents where the rest period is competitive enough with average ionic progress in pulse period. Solving 2nd Order polynomial, we obtain the relationship between idle ratio γ and the dimensionless value t_{ON} . As stated previously, the ions diffuse with respect to $\sim \sqrt{t}$ while they migrate as $\sim t$. Therefore initially, the idle ratio γ decays versus the dimension-less charge period t_{ON} . The saturating behavior indicates that relatively shorter idle ratio is needed to catch up with the applied pulse period during relaxation. With the increase of pulse period t_{ON} and neglecting the lower order effects, we reach the limit $\gamma \propto t_{ON}$, which directly means $t_{OFF} \propto t_{ON}^2$, therefore for higher applied pulse period t_{ON} , the equivalent idle period t_{OFF} for concentration relaxation has to be significantly higher. Such a quickening regime change during higher values of t_{ON} has recently been observed in experimental measurements in which the vertical acceleration of dendrites could be only from role of the electric field [28] (as opposed to diffusion). We should emphasize that the range of typical pulse period is

significantly smaller than the Sand's time previously described in the literature. During that particular time interval, the concentration at the reaction (electrode/dendrite) goes to zero and its length has been compared with diffusion within the entire interelectrode distance. [29] Additionally, the computations are valid as long as the pulse period stays in the multi-collision time lapses ($t_{ON} \gg fs$), as our model is based on coarse time intervals, well in the range of practical pulse charging period. [21, 30]

To summarize, the coarse enough rest period (or fine-enough pulse period) based on equation (8) is recommended for charge relaxation to be competitive with pulse effect on creating inhomogeneous spatial ionic distribution and healthy pulse charging condition via relaxation of concentration gradient. This methodology would effectively prevent the further growth of dendrites.

CONCLUSIONS:

In this paper, we have developed an analytical model for obtaining the most effective square pulse charging parameters for the given electrochemical cell based on the localizations of the ionic concentration and electric field. The dimensional analysis is performed to obtain the critical rest ratio γ , which represents, the idle time period t_{OFF} required for the given corresponding pulse period t_{ON} is represented in terms of cell and solution transport properties. The results are useful for estimating the optimum pulse role on the dendrite-prone electrodeposition on electrode surface, particularly those of involving a packed-structure metal.

References:

- [1] Z. Li, J. Huang, B.Y. Liaw, V. Metzler, and J. Zhang. J. Power Sources, 182 (2014).
- [2] M.A. Rahman, X. Wang, and C. Wen. J of Appl Electrochem 44.1 (2014)
- [3] W. Xu, J. L. Wang, F. Ding, X. L. Chen, E. Nasybutin, Y. H. Zhang, and J. G. Zhang. En & Env Sci, 7,2 (2014).
- [4] Kang Xu. Chemical Reviews, 104,10 (2004).
- [5] F. Orsini A.D. Pasquier, B. Beaudoin, J.M. Tarascon et al. J. Pow Sources, 76 (1998).
- [6] C. Monroe and J. Newman. J. Electrochem Soc 151, 6 (2004).

- [7] C. P. Nielsen, H. Bruus. arXiv:1505.07571, 2015.
- [8] K.J. Harry, D.T. Hallinan, D.Y. Parkinson, A.A. MacDowell, and N.P. Balsara, *Nature materials*, 13,1 (2014).
- [9] J. Steiger, D. Kramer, and R. Monig. *J. Power Sources*, 261 (2014).
- [10] R. Younesi, G. M. Veith, P. Johansson, K. Edstrom, and T. Vegge: 8, 7 (2015).
- [11] R. Khurana, J. Schaefer, L.A. Archer, and G. W. Coates. *J. Am Chem Soc* (2014).
- [12] C. Brissot, M. Rosso, J. N. Chazalviel, and S. Lascaud. *J Power Sources*, 81 (1999).
- [13] I. W. Seong, C. H. Hong, B. K. Kim, and W. Y. Yoon. *Journal of Power Sources*, 178 ,2, (2008).
- [14] A. Aryanfar, D. J. Brooks, A. J. Colussi, and M. R. Hoffmann: *Phys Chem Chem Phys*, 16, 45, (2014).
- [15] A. Aryanfar, D.J. Brooks, A. J. Colussi, B. V. Merinov, W. A. Goddard III, and M.R. Hoffmann: *Phys Chem Chem Phys*, 17,12 (2015).
- [16] C. Xu, Z. Ahmad, A. Aryanfar, V.S. Viswanathan, and J. R. Greer. *PNAS*, 114,1 (2017).
- [17] R. Bhattacharyya, B. Key, H. L. Chen, A. S. Best, A. F. Hollenkamp, and C. P. Grey. *Nature Mat*, 9, 6 (2010).
- [18] S. Chandrashekar, N.M. Trease, H.J. Chang, L.S. Du, C.P. Grey, and A. Jerschow: *Nat Mat*, 11,4 (2012).
- [19] M. S. Chandrasekar, and M. Pushpavanam: *Electrochimica Acta* 53.8: (2008)
- [20] Q. Li, S. Tan, L. Li, Y. Lu, and Y. He: *Sci Adv*, 3,7, (2017)
- [21] A. Aryanfar, D. Brooks, B.V. Merinov, W.A. Goddard III, A.J. Colussi, and M.R. Hoffmann: *J Phys Chem Lett*, 5,10, (2014)
- [22] M.Z. Bazant, B.D. Storey, A.A. Kornyshev: *Phys Rev Lett*, 106,4, (2011).
- [23] D. Aurbach, E. Zinigrad, Y. Cohen, and H. Teller: *Solid State Ionics*, 148, 3, (2002).
- [24] D.R. Ely, A. Jana, R.E. García: *J Pow Sources*, 272, (2014)
- [25] M.Z. Mayers, J.W. Kaminski, T.F. Miller III.: *J. Phys Chem C*, 116,50, (2012).
- [26] R.B. Bird, W.E. Stewart and E.N. Lightfoot. *john wiley & sons*, (1960).
- [27] A. J. Bard, L.R. Faulkner: *Wiley & Sons*, (1980).
- [28] P. Bai, J. Li, F.R. Brushett and M.Z. Bazant. *En & Env Sci*, 9,10, (2016).
- [29] C. Brissot, M. Rosso, J. N. Chazalviel, and S. & Lascaud: *J Pow Sources*, 81(1999).
- [30] J. Li, E. Murphy, J. Winnick, and P.A. Kohl: *J Pow Sources*, 102,1, (2001).