

# **Electrochemical Phase Transformations**

Notes by MIT Student (and MZB)

## INTRODUCTION

Rechargeable Li-ion batteries are secondary batteries that have the Li ions move between the two electrodes upon charging or discharging, hence they are called “rocking chair” batteries. The electrode material in such batteries act as a host to Li ions, where the ions intercalate the crystalline structures of cathode and anode particles. These can accommodate the diffusion of Li ions with minor stress to the crystalline framework like  $\text{Li}_x\text{FePO}_4$  and  $\text{Li}_x\text{C}_6$ . Lithium ions in these electrode particles – mainly nanoparticles of diameter 50 – form a solid solution. However, under certain conditions (of applied potential or current) the homogenous phase can be unstable thermodynamically and the system attempts to lower its free energy by separating into Li-poor and Li-rich phases. This separation occurs when the system (of Li in the particle) lies in the miscibility gap of its free energy  $g(x)$  diagram, Figure 1, and is of two types. Spinodal decomposition, which is where  $g''(x) < 0$ , and nucleation which happens at defects or interfaces due to wetting of such surfaces.

Herein, we consider phase separation for the cases of constant voltage and constant current respectively.

## REGULAR SOLUTION MODEL

The regular solution model for the free energy of mixing is given by:

$$g_{mix}(x) = k_B T [x \ln(x) + (1 - x) \ln(1 - x)] + h_0 x(1 - x)$$

Where  $x$  is the fraction of sites within the electrode nanoparticle that are occupied and  $(1-x)$  is the fraction of holes. The regular solution model considers the Gibbs free energy of the system per site which is comprised of the entropy of the particle (the Li ion)  $k_B T x \ln(x)$ , the entropy of holes  $k_B T (1-x) \ln(1-x)$ , and the enthalpy of particle-hole repulsion  $h_0(1-x)$ , which is the source of immiscibility.

It can be seen in Figure 1 that there is a miscibility gap between the two minima of the free energy. In this regime it is energetically more favorable for the system to phase separate. In the spinodal region, where  $g''(x) < 0$ , a homogenous system is unstable and can decompose into two phases due to thermal fluctuations of the system (as shown later). So it is practically impossible to have a homogeneous system between  $c_{s-}$  and  $c_{s+}$ . However, in the metastable regime, the two regions between  $g'(x) = 0$  and  $g''(x) = 0$ , phase separation occurs only if there are large perturbations in the system such as nucleation at an interface due to surface wetting. Therefore, if carefully designed (i.e. defect free host particles), it is possible to have a homogenous system between  $c_{m-}$  and  $c_{s-}$  or between  $c_{s+}$  and  $c_{m+}$ . The miscibility gap for  $\text{LiFePO}_4$  is between  $c_{m-} = 0.035$  and  $c_{m+} = 0.965$ .

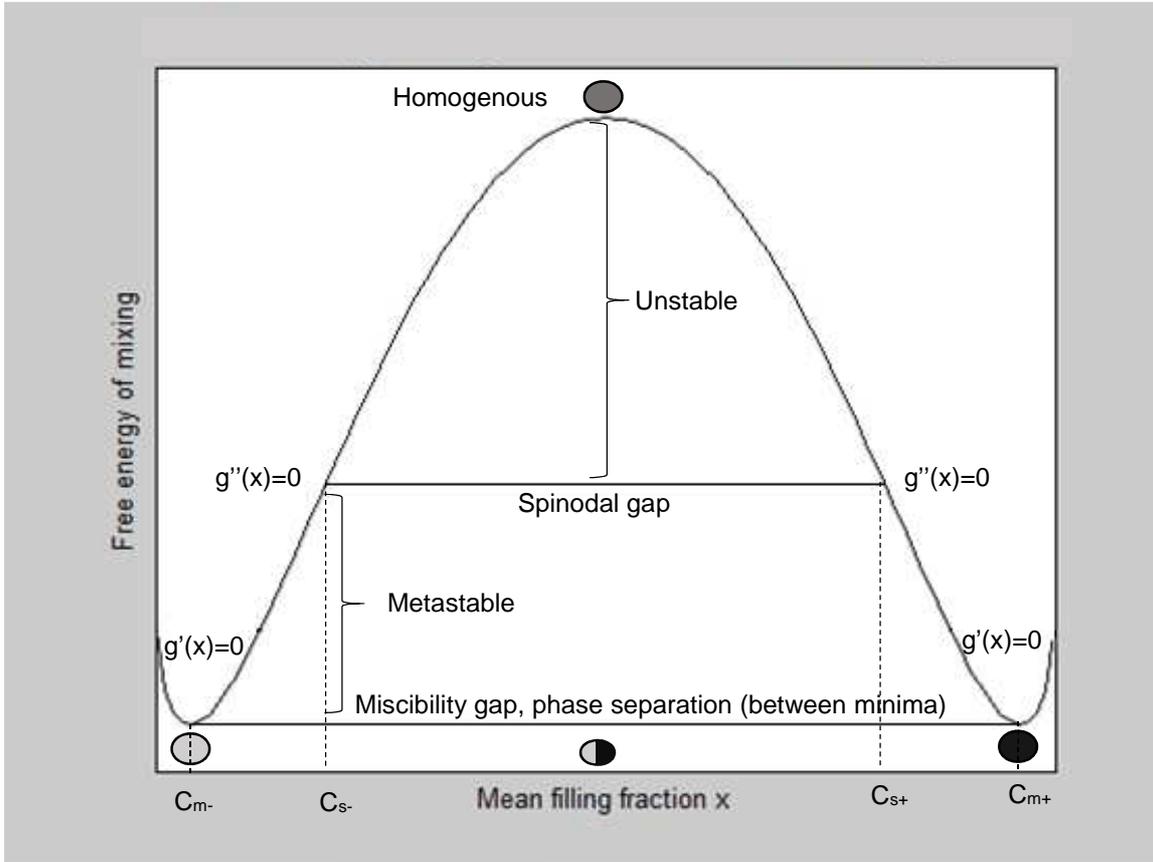


Figure 1: Plot of free energy from regular solution model vs mean filling fraction

By differentiating the free energy with respect to the filling fraction, we obtain the diffusional chemical potential  $\mu(x)$ , Figure 2:

$$\frac{\partial g}{\partial x} = \mu(x) = k_B T \ln\left(\frac{x}{1-x}\right) + h_0(1-2x)$$

The open circuit voltage (OCV), Figure 3, is given by:

$$V_o = V^o - \frac{\mu}{e} = V^o - \frac{k_B T}{e} \ln\left(\frac{x}{1-x}\right) - \frac{h_0}{e}(1-2x)$$

The voltage is the change in the free energy of the system, shown earlier, per addition (or removal) of Li ion from the electrode, which is related to number of electrons transferred from cathode to anode. When  $h_0$  is greater than  $2k_B T$  (the critical mixing enthalpy), phase separation is observed, as shown in previous lecture notes.

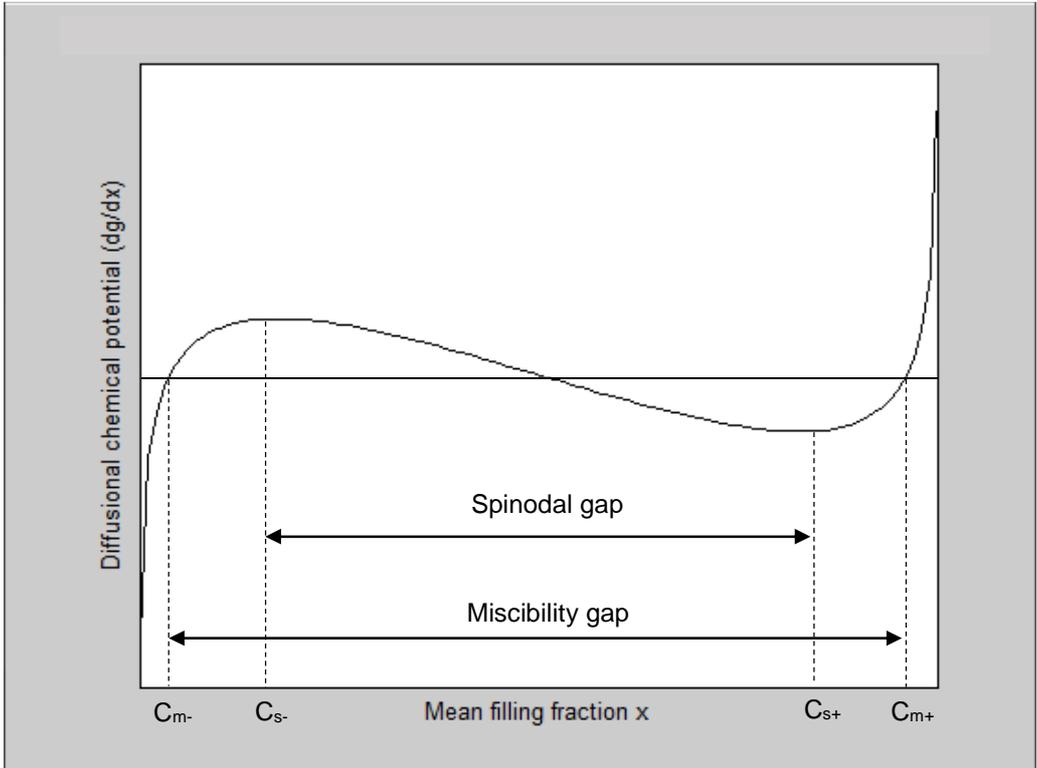


Figure 2: Plot of diffusional chemical potential vs the mean filling fraction

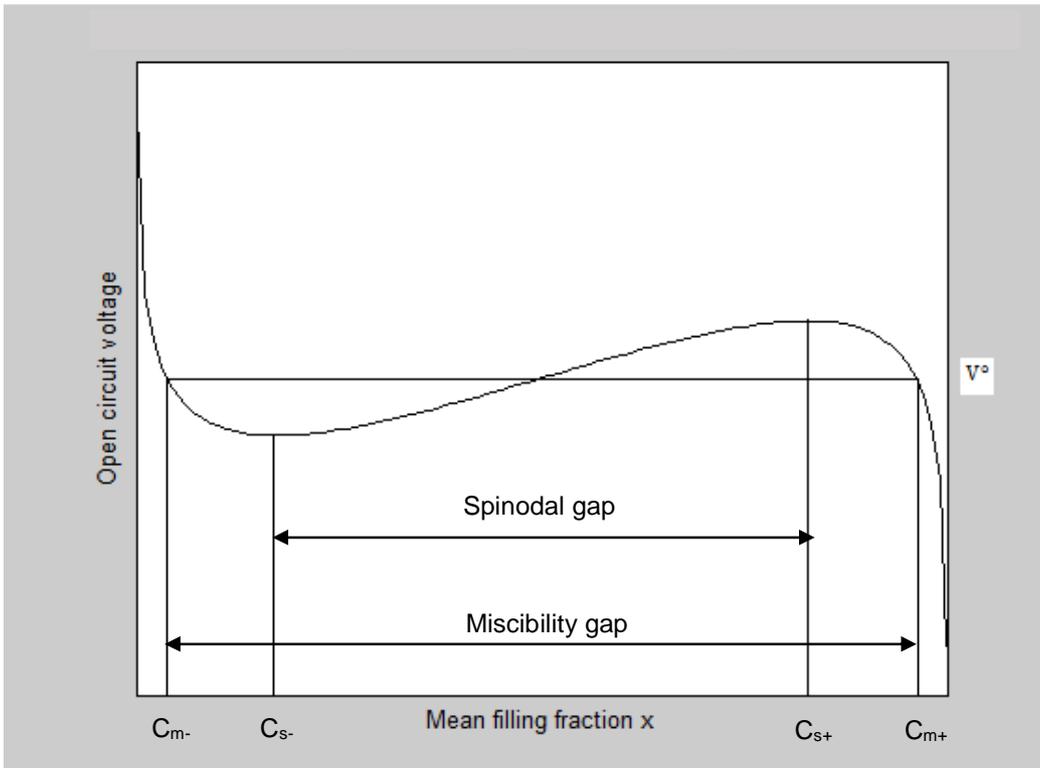
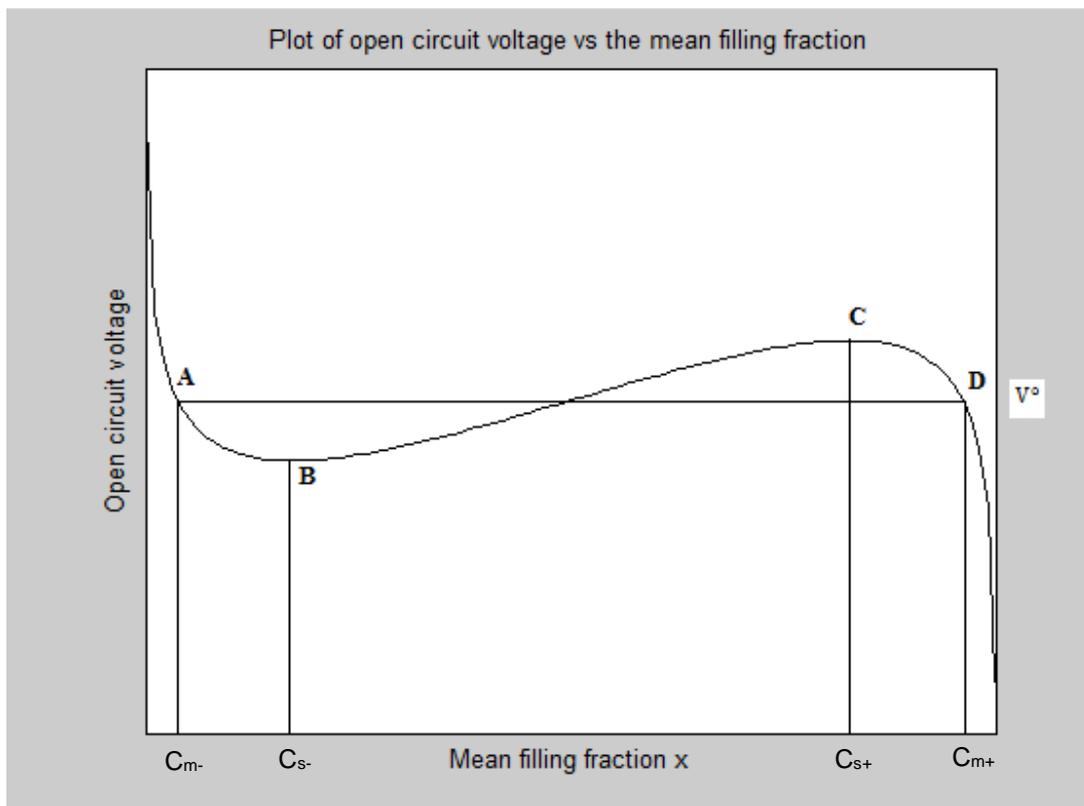


Figure 3: Plot of open circuit voltage vs the mean filling fraction

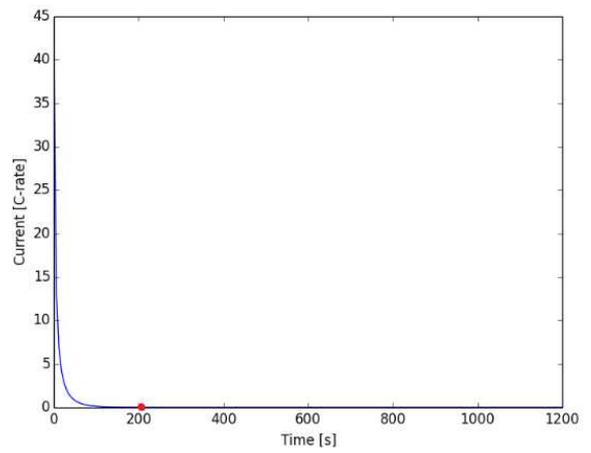
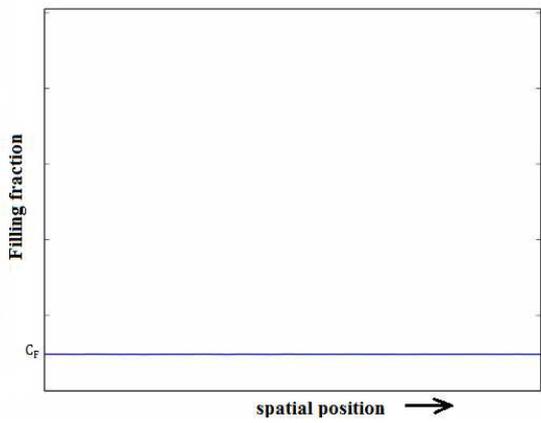
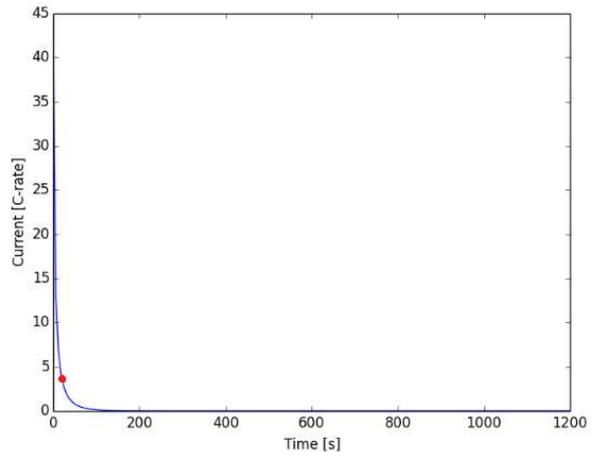
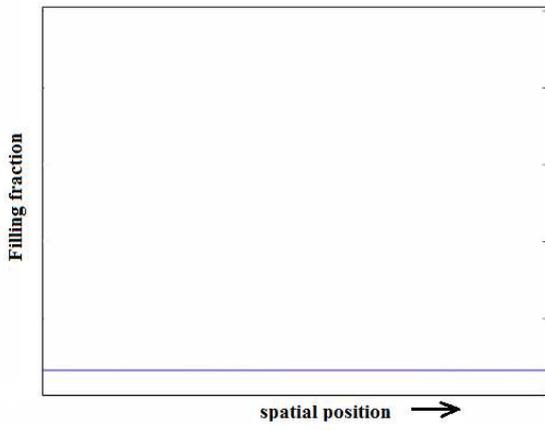
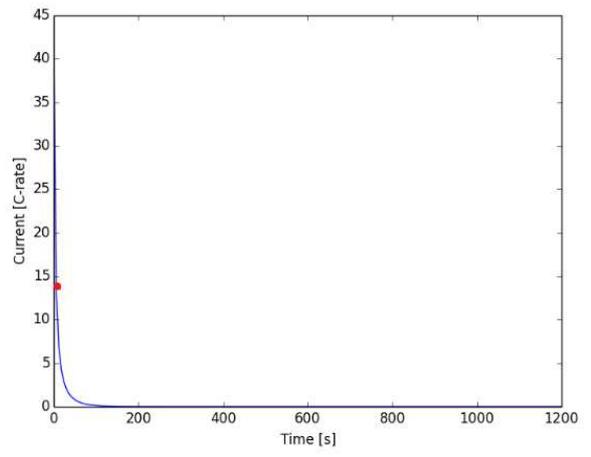
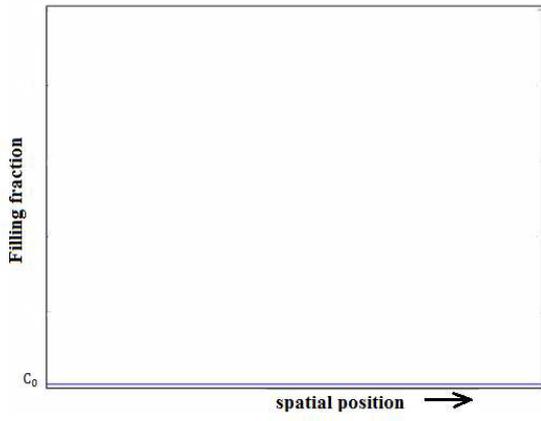
### PHASE SEPARATION AT CONSTANT VOLTAGE:

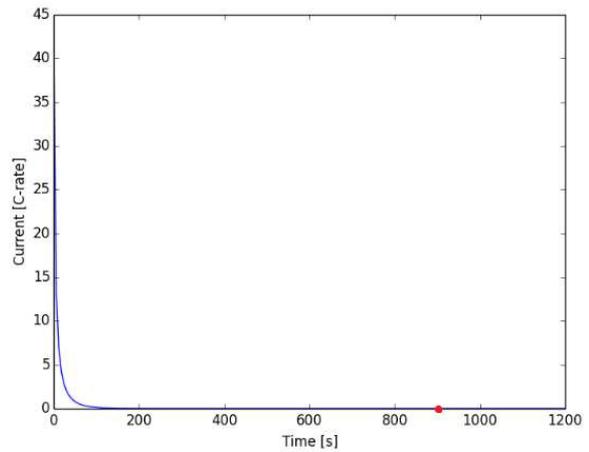
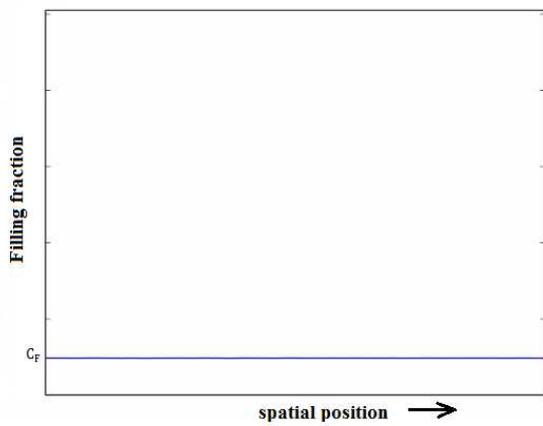
Consider the case of systems which exhibit phase separation ( $h_0 > 2k_B T$ , according to the regular solution model). In the voltage versus filling fraction graph (which is equivalent to plotting the voltage versus the state of charge), the regions to the left of point A (filling fraction  $C_{m-}$ ) and to the right of point D (filling fraction  $C_{m+}$ ) correspond to a single homogeneous phase. The region between B and C is unstable. If the overall composition is such that “x” lies between these two points, the slightest perturbation will cause the system to split into two phases corresponding to points A and D (in such a proportion that the overall composition still remains “x”). A single phase with composition lying between B and C will never be observed in practice. The regions AB and CD are metastable regions and the system is stable to small perturbations in this region. Large perturbations will cause the system to phase separate, provided nucleation is possible.



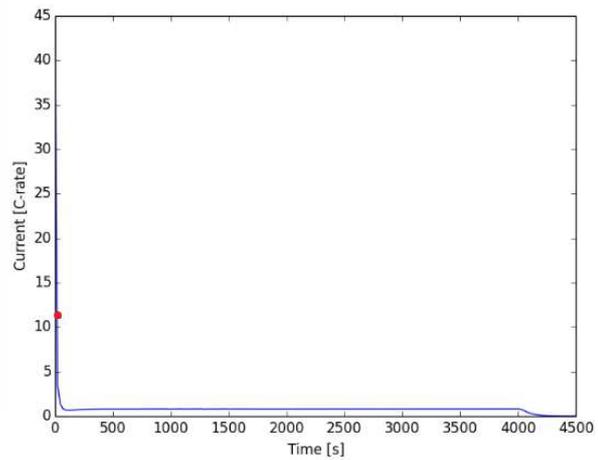
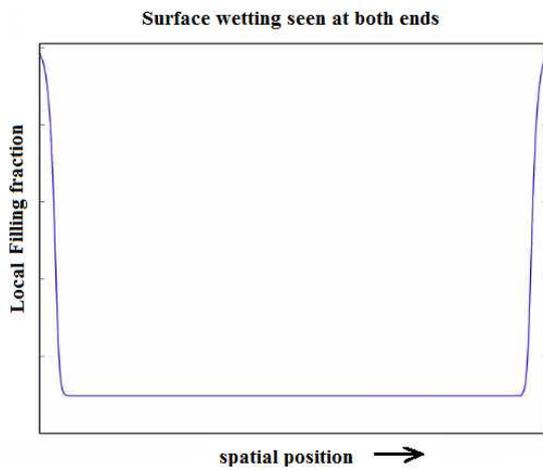
To study phase separation at different constant voltages, PITT (Potentiostatic Intermittent Titration Technique) is performed. In this, we start at the open circuit voltage at a small filling fraction. Then a potential step is given and the system is allowed to relax, as shown below. Initially (before entering the metastable region), the system continues to remain as a single homogeneous phase after each voltage step and relaxation.

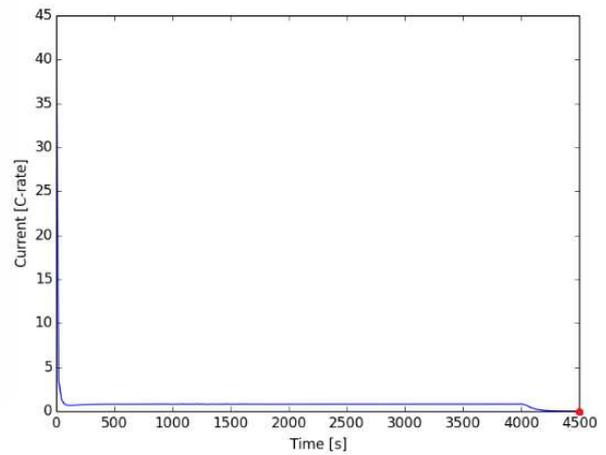
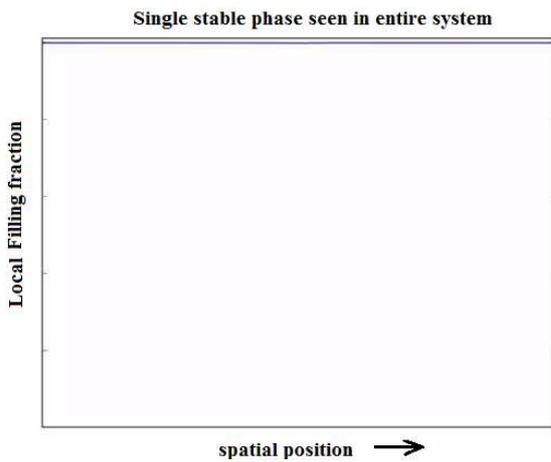
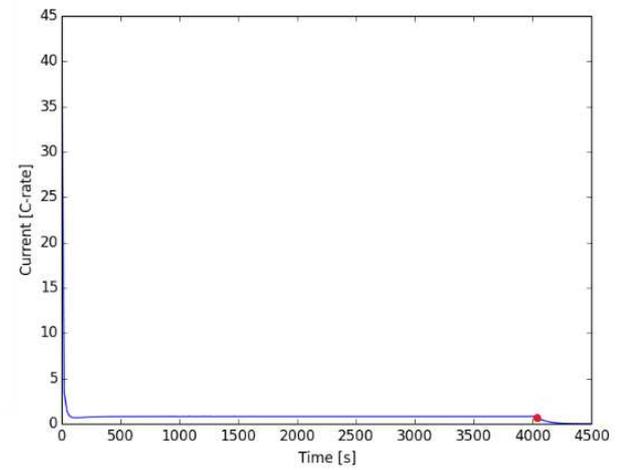
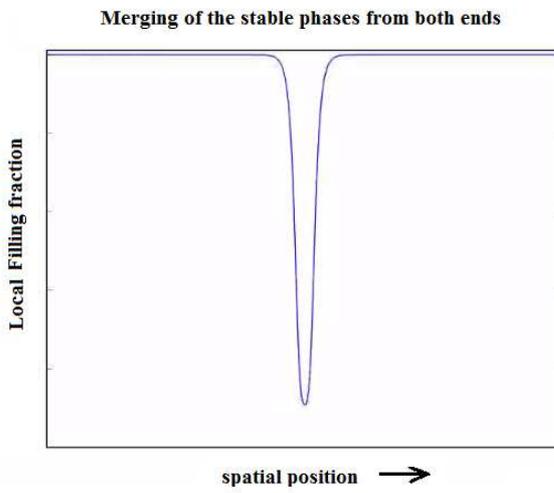
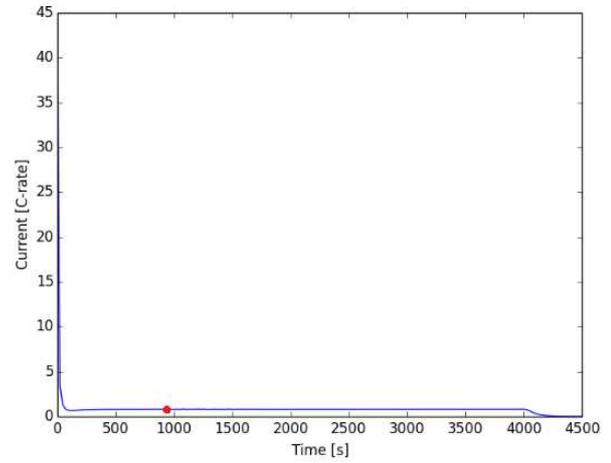
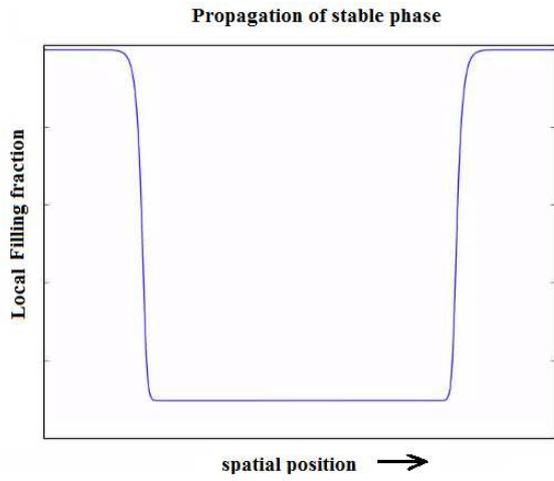






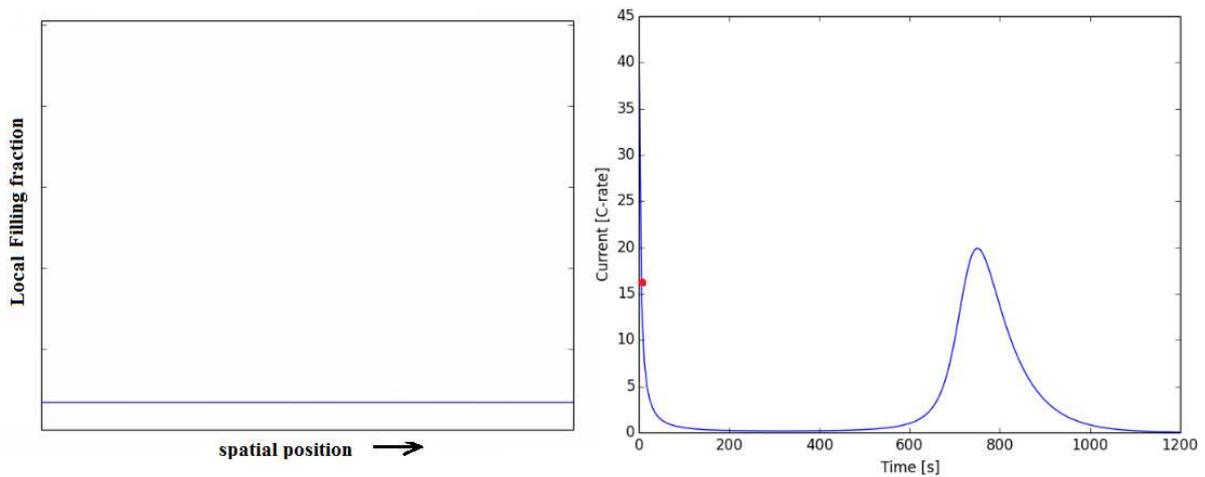
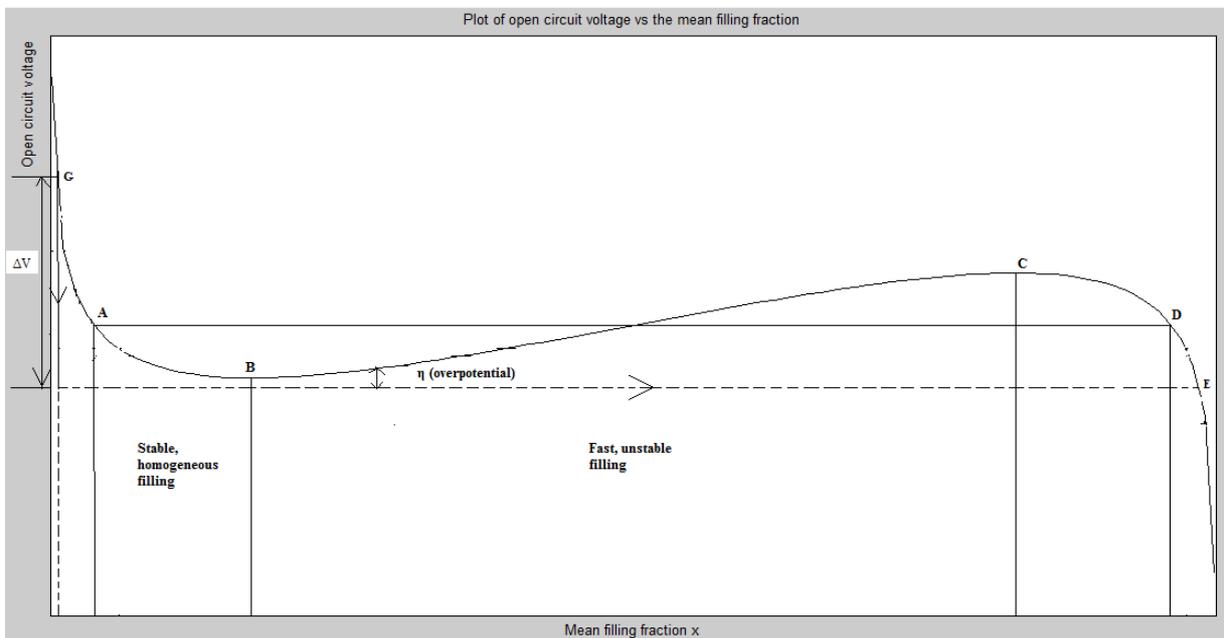
In the next simulation, the same voltage step (which brings the system into the metastable region) is given, but this time a large perturbation is given. One example of a large perturbation is surface wetting which promotes nucleation. The concentration in most of the medium corresponds to the metastable filling fraction ( $C_F$ ) at the given voltage. At the surface, the filling fraction is equal to the value on the stable arm on the right for the given voltage ( $C_E$ ). This acts as a large perturbation and drives the entire system from the metastable region to the stable filling fraction.

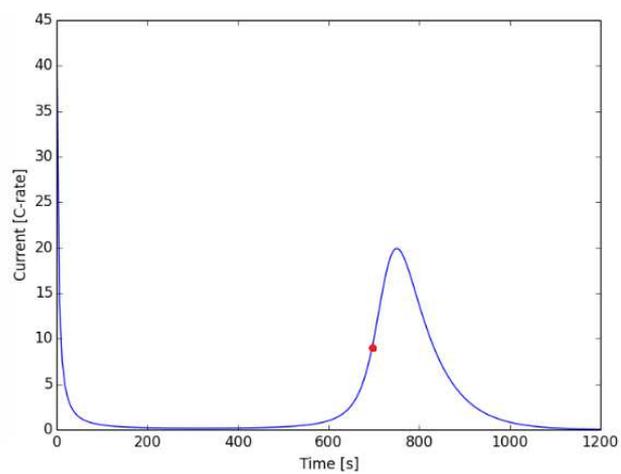
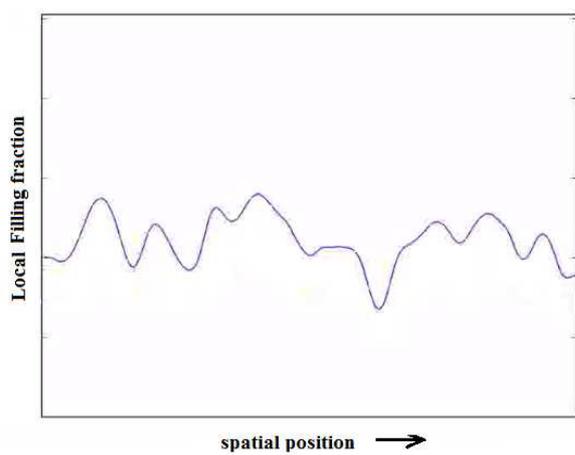
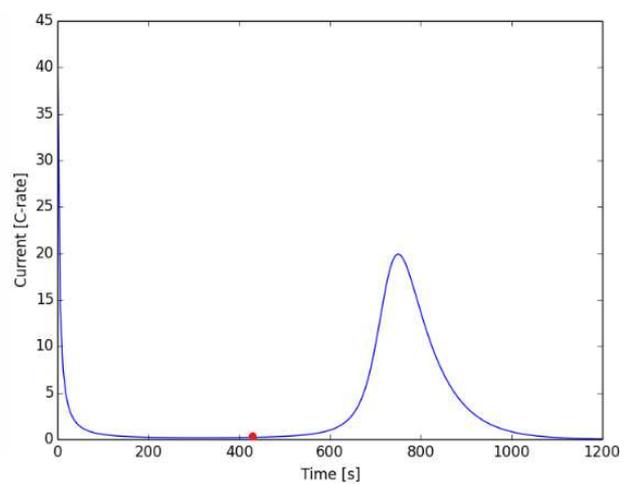
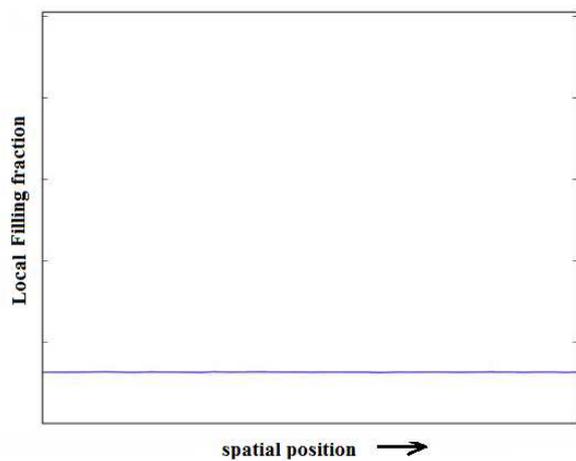
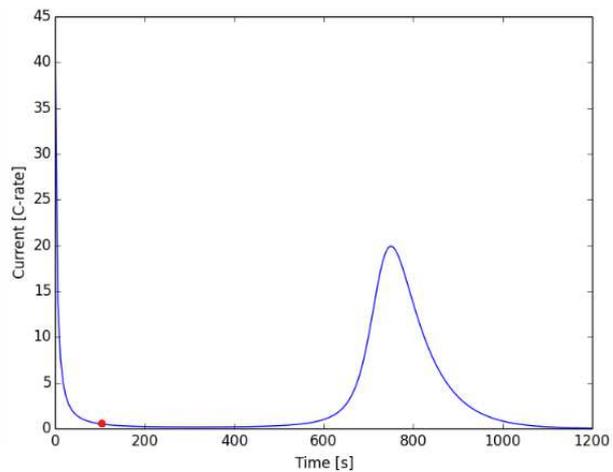
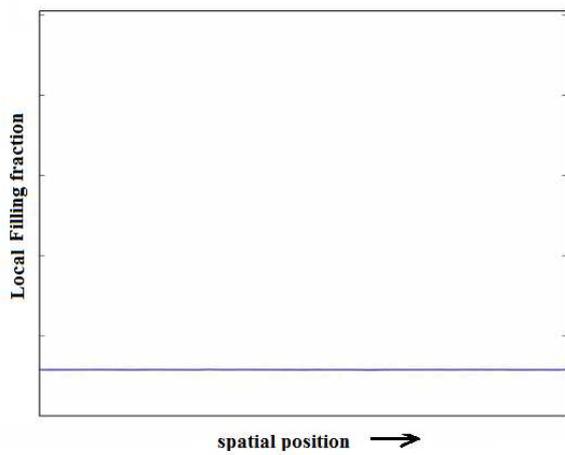


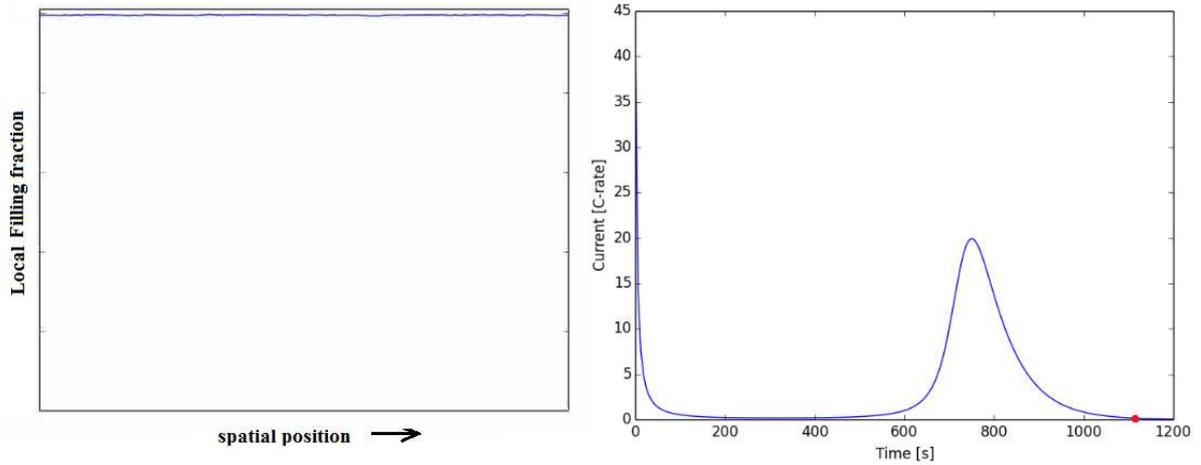


The above discussion has summarized the behavior in the metastable region both in the presence and absence of nucleation. Next, we discuss spinodal decomposition, which is seen when the voltage is taken below the minima on the left side of the voltage vs filling fraction curve (i.e.,

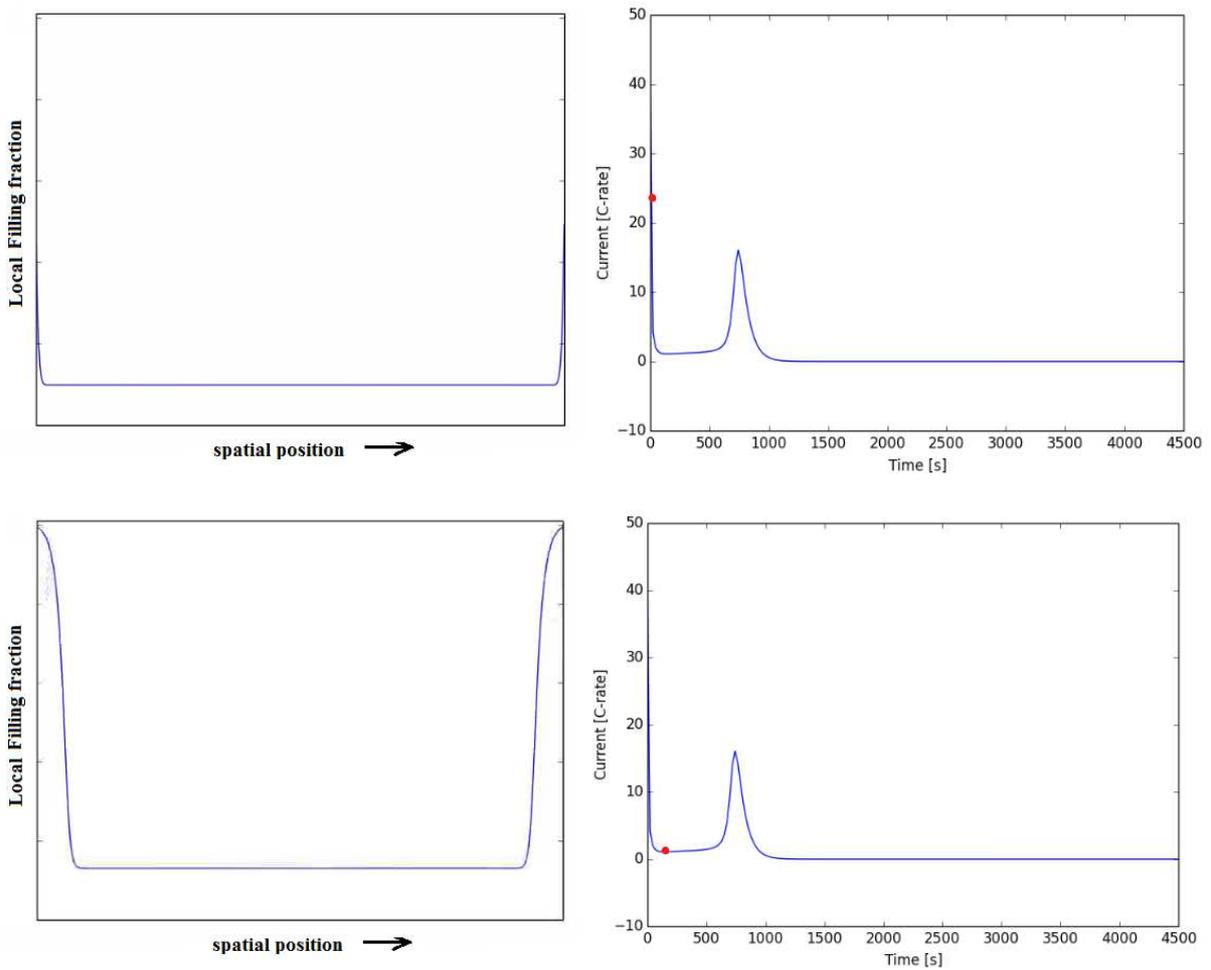
below the voltage corresponding to point B). Initially, the voltage is taken to a value that is only slightly lower than the value corresponding to B. There will be slow homogeneous filling until the filling fraction is equal to the value corresponding to point B. Close to point B, the filling will be extremely slow because the driving force, which is the overpotential, is very small. This can also be seen on the current vs time plot, where a constant low value is observed before the large peak. Then all of a sudden, very fast and unstable filling is observed as the system quickly jumps to the stable arm on the right. This corresponds to the large peak on the current vs time plot. This process takes place even if nucleation is not feasible for the system. As the system crosses point B, the driving force (the overpotential  $\eta (=V-V_{OCV})$ ) starts increasing, which further promotes quick movement to the stable phase on the right arm. The graphs below show this process in the absence of surface wetting (i.e., in the absence of nucleation).

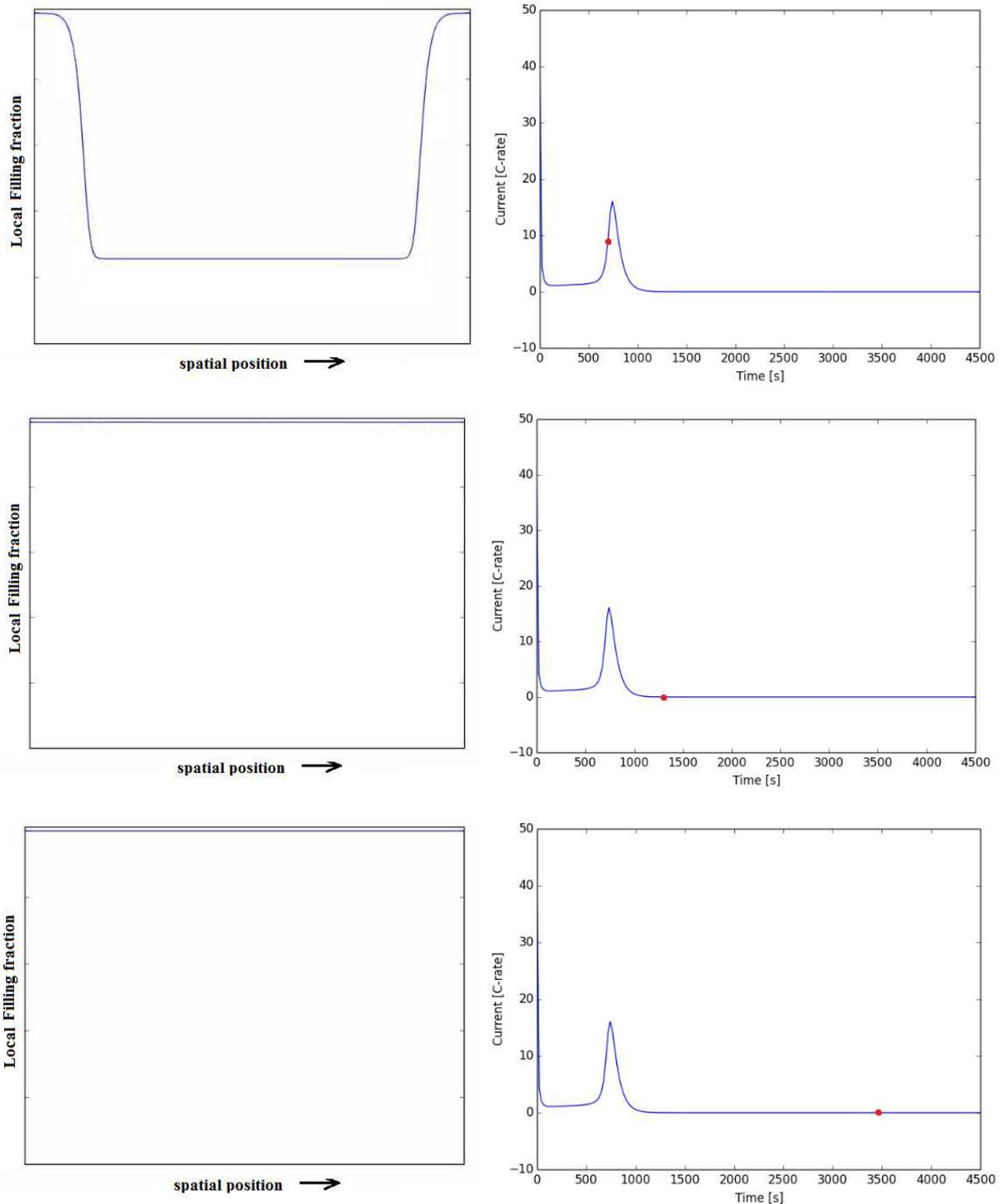






The following series of graphs illustrate the same spinodal decomposition process as above, but now in the presence of surface wetting. It is observed that the presence of nucleation has the effect of accelerating the entire process.





The above discussion was for the case where the voltage was only slightly below the minima on the OCV curve. When the voltage step is very large, and the voltage is much lower than the voltage at B, the overpotential (which is the driving force) is very large. The system will then jump quickly to the stable phase and the slow homogeneous filling we see above will not be observed.

## PHASE SEPARATION AT CONSTANT CURRENT:

In the voltage against filling fraction plot, Figure 4, it can be seen that when the voltage decreases the system hits a plateau, which is where the phase separation occurs. At this point, there is a number of possible paths that the system can take. If the voltage decreases slowly, path A, and there is no nucleation in the system, it is possible to enter the metastable regime and have a homogenous system up to  $c_{s-}$ , but this soon spontaneously collapses into two separate phases due to fluctuations (perturbations) in the system and the voltage jumps to the plateau, this is known as spinodal decomposition. Another possibility is that as the voltage decreases, interfacial tension between stable phases (the host particle facet boundary and the lithiated phase) promotes surface wetting which nucleates and propagates the high density phase, path B.

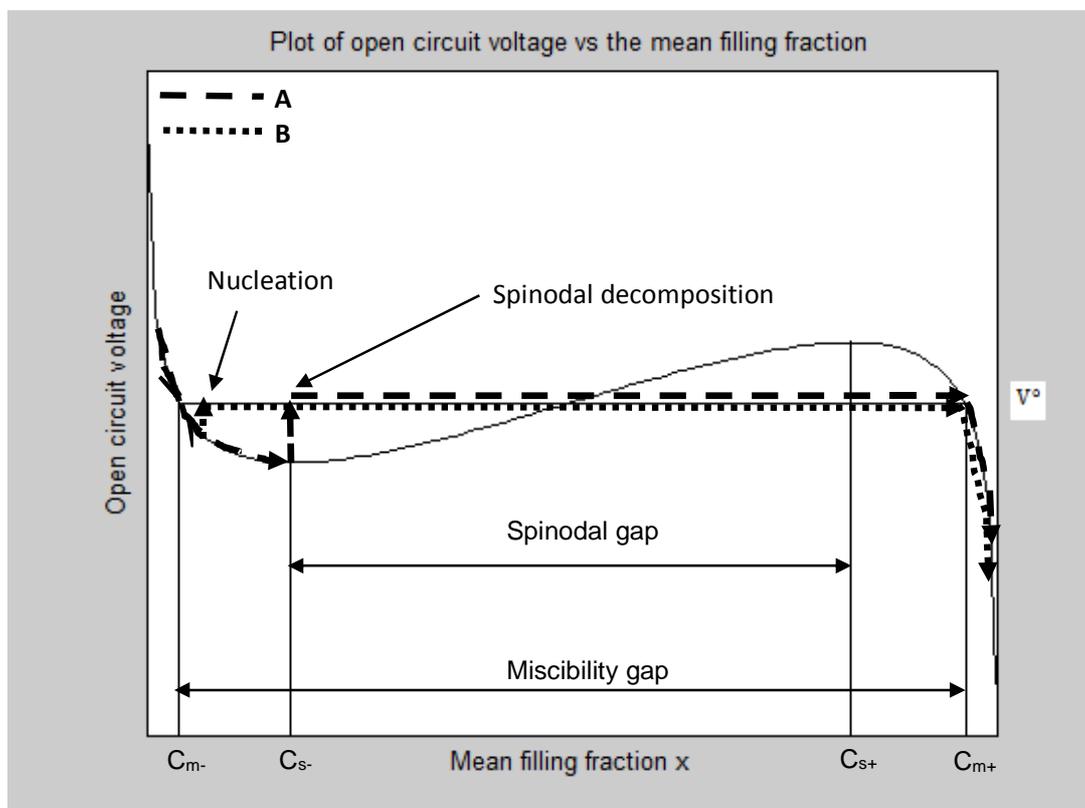
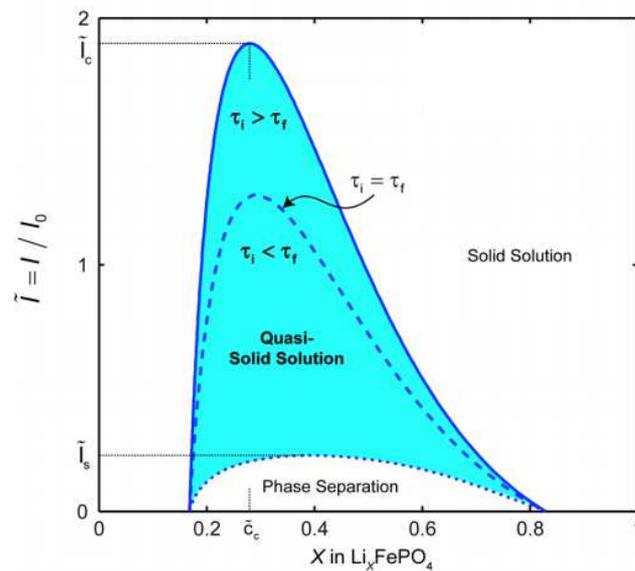


Figure 4: Discharging phase separation pathways: Spinodal decomposition (A) and Nucleation (B)

However, at higher currents, when the system is reacting in the bulk (a homogeneous reaction), the current can actually suppress the phase separation because the system doesn't have time to respond and go through the spinodal decomposition process before the particle fills completely. This can be investigated using linear stability analysis, and the result indicates that, for low enough currents, the system has time to undergo spinodal decomposition and will do so upon reaching the spinodal gap. However, because that leads to small phase fronts where the remaining reaction can

occur (see Figure 7), this is not favorable at high currents. Instead, it can be shown that at high currents, the system is linearly stable to concentration fluctuations, and the particle fills homogeneously as a solid solution. The results of such a linear stability analysis for a simple model of  $\text{LiFePO}_4$  are shown in Figure 5 (Bai, P., Cogswell, D., Bazant, M. Z. *Nano Letters* 2012). Because higher currents lead to homogeneous filling, voltage curves can resemble the non-monotonic homogeneous voltage curve above. In Figure 6, simulated results of constant current discharge are presented. This is effectively done by adjusting the potential difference at each time step to maintain the desired current. The results presented in Figure 6 are simulated in the absence of any nucleation, i.e. phase separation occurs only as a result of spinodal decomposition which happens due to thermal fluctuations in the system (simulated here by Langevin noise).



*Figure 5: Spinodal and Phase Separation envelopes*

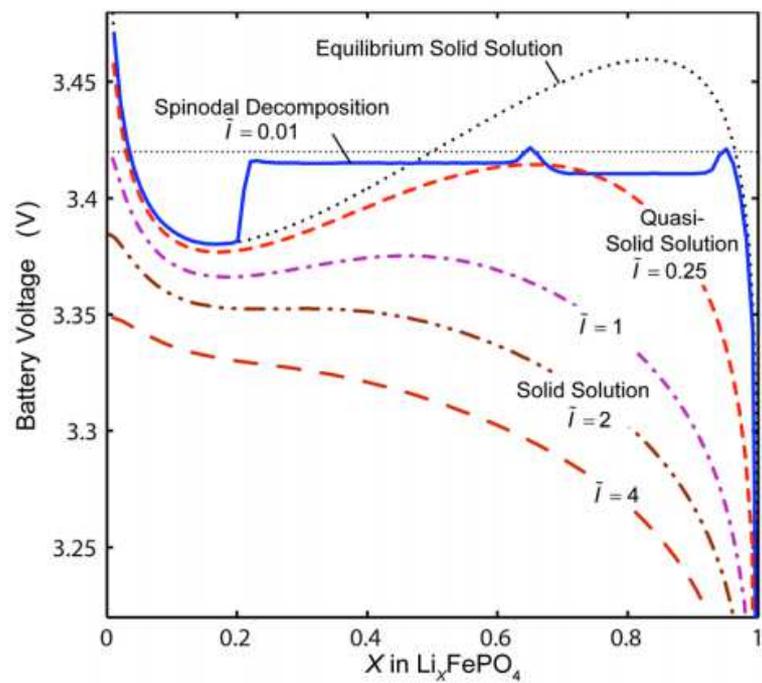
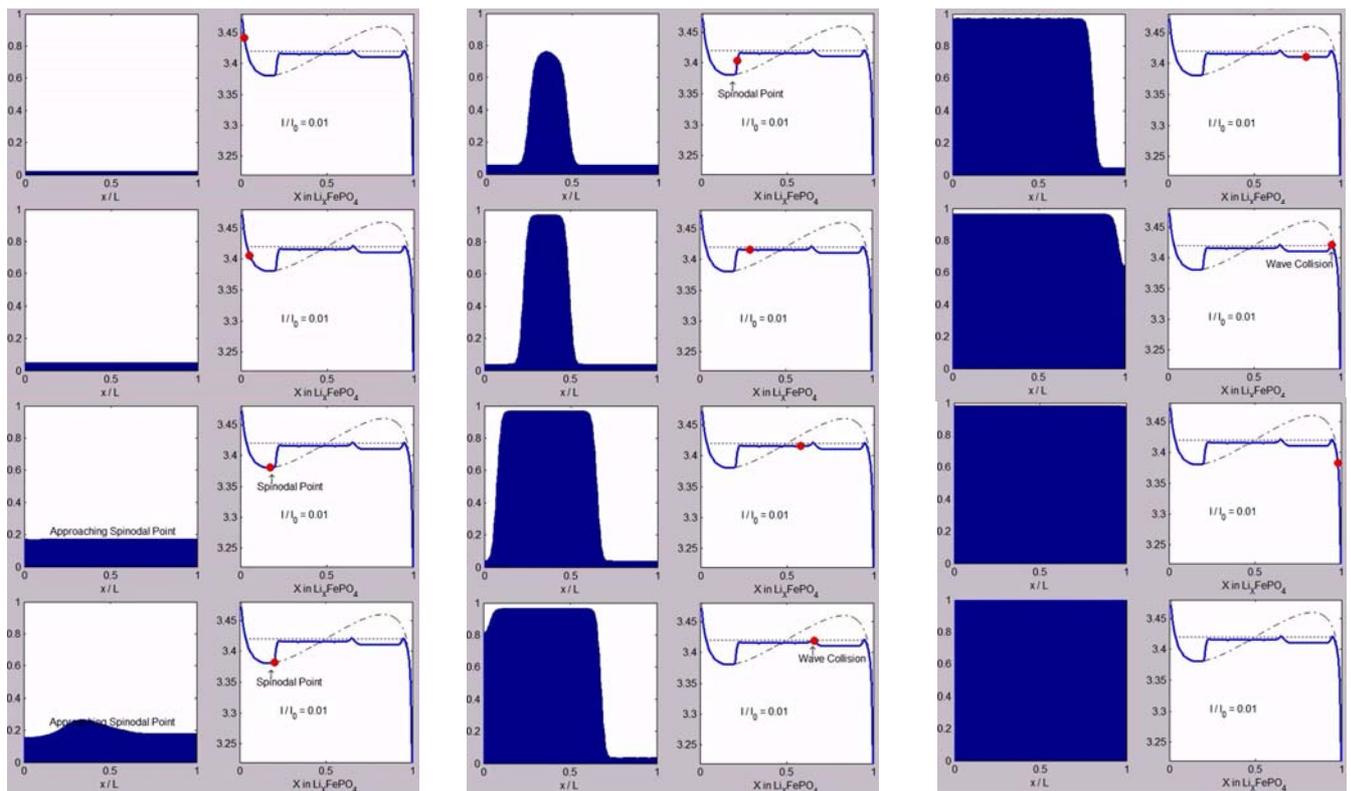


Figure 6: Discharging V-x relations at different currents in the absence of nucleation

The spinodal decomposition at a small current (smaller than transition current  $\tilde{I}_s$ ),  $\tilde{I}=0.01$ , is similar to that described earlier for the equilibrium OCV case. The voltage decreases as intercalation of Li ions fills the system up to the spinodal point of  $c_s$ , after which it spontaneously separates into lithium rich and lithium poor phases on the equilibrium plateau, triggering two intercalation waves that propagate through the host particle, 5<sup>th</sup> in Figure 7. The decomposition takes place with a slight overpotential (deviation from the equilibrium OCV) due to the kinetic resistance of the intercalation waves. The small bumps shown on the spinodal decomposition curve are the result of the annihilation of the intercalation waves at the particle facet boundaries. After the first waves annihilates, 9<sup>th</sup> in Figure 7, the overpotential doubles since two waves are replaced by one,  $\tilde{I}=0.01$  curve in Figure 6.

Figure 7, demonstrates lithium filling across a host particle of length  $L$  with time. The graphs on the left plot the local lithium filling fraction (local to the particle) against the length of the particle. Initially, the fraction of lithium is uniform throughout the particle, but after the spinodal decomposition, a lithium rich phase emerges with two lithium poor phases on the sides. The Lithium rich phase then propagates as two waves (one from each side) through the particle as more lithium enters the particle.



**Figure 7: Spinodal decomposition at  $\tilde{I}=0.01$  and the propagation of Lithium rich phase across the length of the host particle with time. The graphs on the left plot the local lithium filling fraction in the particle against the length of the particle, while the graphs on the right plot the voltage of the system against the average filling fraction in the particle. The red dot shows the variation in the system voltage with time**

At larger applied currents, the spinodal decomposition is suppressed and the filling fraction of lithium in the particle increases more or less uniformly forming a homogenous solid solution or quasi-solid solution of concentration that increases with time. At  $\tilde{I}=0.25$  some instabilities tend to phase separate the system. However, the kinetics of filling the system are faster than the rate of phase separating instability propagation, therefore such “attempts” are suppressed as shown in Figure 8.

At currents much larger than the transition current  $\tilde{I}_s$ , lithium filling is homogenous and uniform, a perfect solid solution of increasing concentration is formed as the particle gradually hosts more lithium, Figure 9.

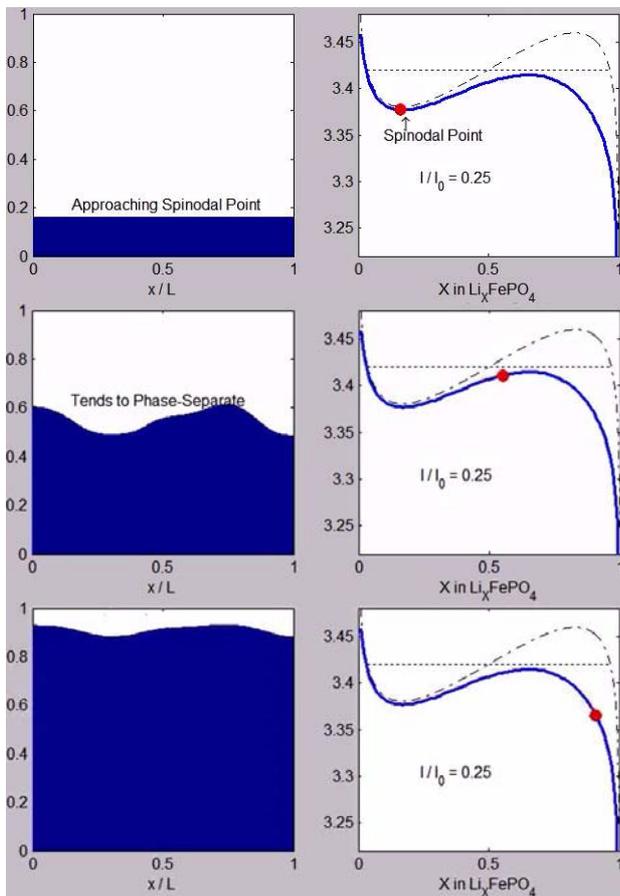


Figure 8: Discharging at  $\tilde{I}_s=0.25$  in the absence of nucleation

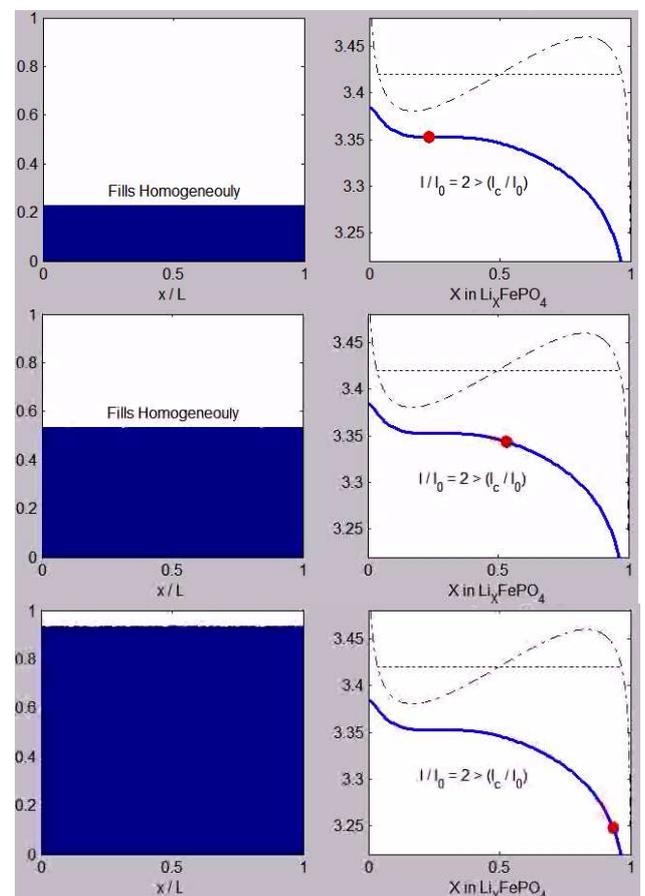


Figure 9: Discharging at  $\tilde{I}_s=2$  in the absence of nucleation

To better model experiments, which suggest the wetting of the facets of the particle by lithium-filled phases, simulations which allow boundary wetting are performed. At currents lower than transition current  $\tilde{I}_{s0}$ , such heterogeneous nucleation triggers phase separation when the system is in the miscibility gap, well before the spinodal filling fraction  $c_s$  is reached, Figure 10. Nucleation is a much stronger perturbation than thermal fluctuations, therefore, it nudges the system to the equilibrium phase separation plateau even in the metastable regime. Here too, two waves of lithium

rich phases are propagated, but in this case, at the boundaries. These waves later merge, as shown in Figure 11.

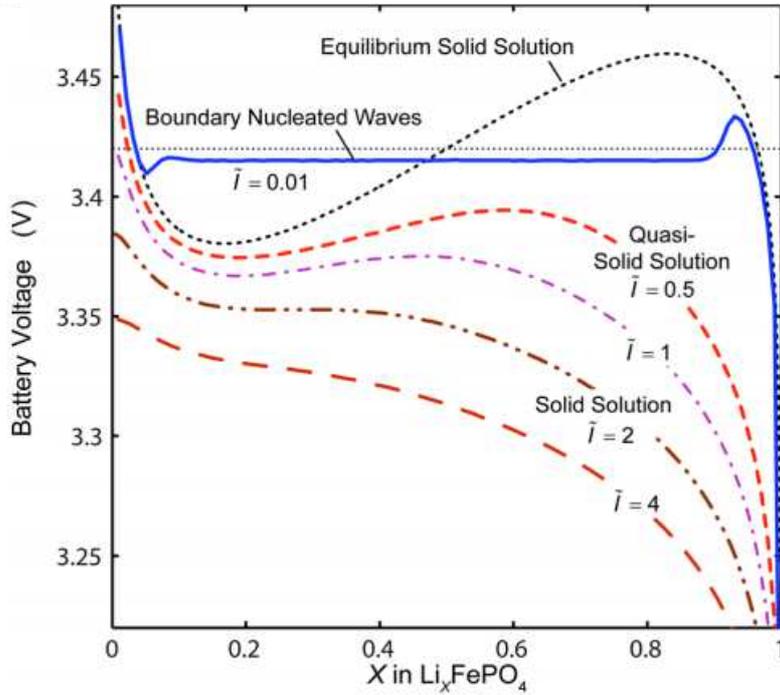


Figure 10: Discharging  $V$ - $x$  relations at different currents in the presence of nucleation

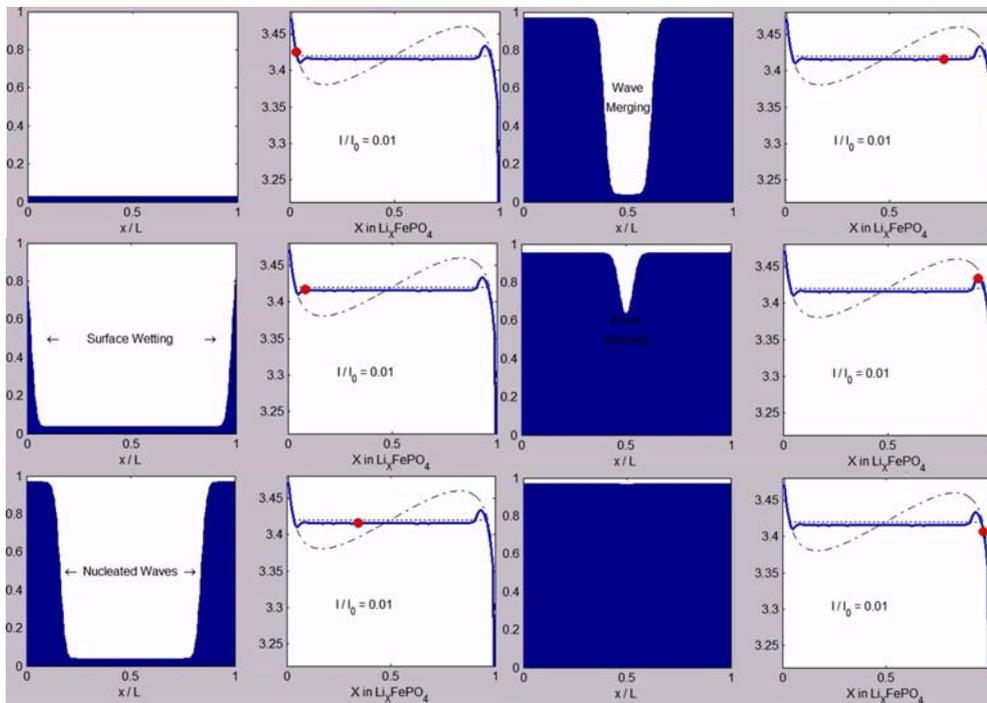


Figure 11: Discharging at  $\bar{I}_s=0.01$  in the presence of nucleation

At currents higher than  $\tilde{I}_s$ , the boundary wetting does not perturb the system enough to phase separate, and the filling fraction at the center of the particle increases uniformly, Figure 12.

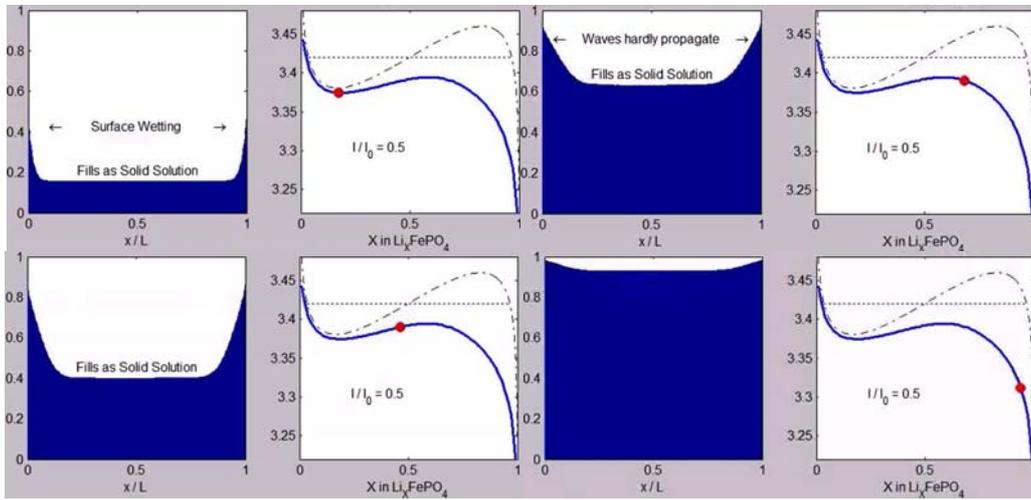


Figure 12: Discharging at  $\tilde{I}_s=0.5$  in the presence of nucleation

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