

An Introduction to Phase-Field based Model for Predicting the Baking Level of Carbon Anodes

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Abstract

The baking of carbon anode in furnace is a vital step in the carbon anode production cycle for aluminium industry. The green (unbaked) anodes so formed by compaction of recycled anode butts, coal tar pitch and coke do not possess the required material properties that are desirable during the utilization of carbon anodes in the electrolysis cell. The baking process transforms green anodes into baked anodes to achieve these desirable properties to ensure the anodes withstand the harsh thermal and electrochemical conditions of the electrolysis cell. Therefore, predicting the baking level of carbon anode is of paramount importance. In the present study, a thermodynamic and phase-field theory (a mathematical technique for solving interfacial and phase transformation problems) based model has been employed for prediction of baking level of carbon anodes during baking. A physically-based internal state variable describing the baking level is proposed which determines the extent of baking level achieved at a prescribed location and time in the anode pack. A time-dependant and temperature driven evolution equation for the baking level is employed using thermodynamics and phase-field based model. A brief discussion on the application of developed model for prediction of material properties evolution during the baking process is also presented.

Keywords: Anode-baking, baking level, temperature driven transformation, solid-solid transformation, evolution of material properties.

1. Introduction

Carbon Anode Baking is one of the most important step in Aluminium production. The term 'Green anode' refer to the un-baked anode formed by mixing and vibro-compacting the ingredients i.e. calcinated petroleum coke, recycled anode butts from reduction cell and coal tar pitch to form a compact solid block. The so formed un-baked anode is then baked and subsequently consumed as anode in the electrolytic cell for Aluminium reduction. The chemical and thermal conditions in electrolytic cell are quite severe that can cause thermal shock, anode cracking and other undesirable effects. The green anode does not possess the required thermal and mechanical characteristics that are of paramount importance for usage in electrolytic cell. The malfunctioning of a carbon anode in a reduction cell can have drastic impact on operational continuity of an electrolytic cell. In worst case, it can crack and fall into the liquid bath of the cell leading to operational and production delays. Other direct and indirect effects may include, but are not limited to, over-consumption, dusting, and decrease in electrical current efficiency. To overcome these effects, baking of the green anode is carried out in a furnace that changes the thermo-electro-mechanical behavior of the anode making it suitable for use in the electrolytic

cell. Both over-baked and under-baked anodes are undesirable. It is therefore of vital importance to understand the extent of baking level at any time.

The anode baking process is indeed a solid-solid phase transformation (PT) process whereby a green anode (initial phase) is transformed into a baked anode (final phase). This PT is a second-order continuous transformation and no latent heat is involved in the transformation from green to baked anode and that there is a large temperature difference involved between the two phases. Physically, a second-order continuous transformation may be viewed as a phenomenon where the transition from one phase to another is taking place very smoothly without changing the thermodynamics abruptly. The baking process is essentially thermally driven as during the baking process, green anode is subjected to significant temperature change for a very long time. Hence, a suitable temperature driven solid-solid PT model can quite accurately simulate the baking level of carbon anode. Such models can be accurately developed using the Phase field theory (PFT) and the models so developed are called Phase field models (PFM) [1].

PFT has been evolved greatly over the last few decades. PFT was principally developed to solve interfacial problems like solidification. The origin of PFT dates back to the work of van der Waals who developed a density based PFM for liquid-gas system. PFT since has been applied to a variety of microstructure transformation problems like solidification dynamics, solid-solid transformation, coarsening, grain growth, dislocation dynamics, and crack propagation [2]. As a first step, PFM introduces a phase-field parameter which takes discrete value in bulk phases. For example, in solidification problem, the phase-field can assume a value of 0 in one phase (solid) and a value of 1 in the other phase (liquid). At the liquid-solid interface, the value of phase field can be assumed to vary smoothly from 0 to 1 (a diffuse interface model) or sharply (sharp interface model). Secondly, a thermodynamic free energy (or entropy) functional is developed that is a function of phase-field and the microstructure transformation parameters like temperature, strain etc. The variational derivative of thermodynamic free energy functional with respect to the phase-field provides the necessary driving force for the phase transformation. Finally, an equation for evolution of phase-field is developed to keep the track of evolution of the phase-field. The famous time-dependent Ginzburg-Landau equation [3] is utilized for the evolution of phase-field with respect to time.

In the context of anode baking as discussed previously, one can distinguish two distinct phases at the start and end of the baking process i.e. the green/unbaked and baked. Since the baking process is essentially temperature driven, a thermodynamic and phase field based free energy functional dependent on baking level (phase-field) and temperature can be developed and utilized to predict the evolution of baking level with time. In the existing literature on PFT, Levitas and Preston [4] have already developed free energy functional for temperature driven martensitic transformation (MT). MT is the process whereby Austenite phase of steel is converted to Martensite phase. The MT can be induced by changing the temperature (on cooling) or by applying an external stress. Reverse transformation can be achieved by heating Martensite to form Austenite. Since MT and anode baking have analogies i.e. both are solid-solid temperature driven PT processes, the already developed function as mentioned in research work [4] was selected and tailored for anode baking process; owing to the analogies mentioned. The free energy functional is:

$$F(T, \phi) = \frac{1}{2} A \phi^2 + (3\Delta G^T - A) \phi^4 + \frac{1}{2} (A - 4\Delta G^T) \phi^6 \quad (1)$$

where: $F(T, \phi)$ Free energy functional, J/m³

T Anode absolute temperature, K

ϕ Baking level, fraction

ΔG^T Temperature based Gibb's free energy, J/m³
 A Temperature dependant linear function, J/m³

In addition, the equations for ΔG^T and A are as under:

$$A = T - T_c \quad (2)$$

and,

$$\Delta G^T = \frac{1}{3}(T - T_e) \quad (3)$$

where: T_c Critical temperature, K
 T_e Equilibrium temperature, K

For the critical temperature, it is the temperature below which the initial unbaked phase is stable. It is understood that the baking process is started so as the anode is placed in the pit, so anode initial temperature itself is taken as the critical temperature i.e. 50⁰C. For the equilibrium temperature, it is the temperature at which both the unbaked and baked phases are in equilibrium. Owing to the fact that the marked difference in unbaked and anode properties can be attributed to the onset of volatile release, the start of volatile release temperature i.e. 250⁰C was taken to be the equilibrium temperature. It is however, imperative to mention that exact values of these temperatures need to be evaluated experimentally by analyzing the microstructural changes that occur during the baking process.

The evolution of baking level is governed by time-dependent Ginzburg-Landau equation:

$$\frac{\partial \phi}{\partial t} = -L \frac{\delta F}{\delta \phi} \quad (4)$$

where: L Kinetic co-efficient, m³/J.s
 $\frac{\partial \phi}{\partial t}$ Time rate of change of baking level, s⁻¹
 $\frac{\delta F}{\delta \phi}$ Variational derivative of free energy functional, J/m³

The value of kinetic co-efficient represents the speed of transformation. It should be noted that since the MT is a rapid one because of quenching, the value of L is 1 (high) [4] but for the case of anode baking the value of L as iteratively calculated from simulation came out to be 2x10⁻⁸ which is very small. This was expected as the MT is completed in a very short interval of few seconds whereas the baking process takes almost 240 to 360 hours (including cooling time). $\delta F/\delta \phi$ represents the variational derivative of free energy functional which can be calculated using variational calculus based equation mentioned in [4].

2. Model and computational method

2.1. Geometry and Meshing

Commercially available Multiphysics software COMSOL was utilized for simulating the PFM. A small 2D square domain (0.1m x 0.1m) was modeled as carbon anode. The domain was finely meshed with the mesh size being 24916 cells and average element quality being 0.9942. The modeled geometry and meshed are shown in Figure 1. Since this study focuses only on the effect of temperature application on carbon anodes, detailed 3D modelling of anode along with the modelling of complete pit and flue walls is not required. The history of anode temperature profile is sufficient for simulating the PFM.

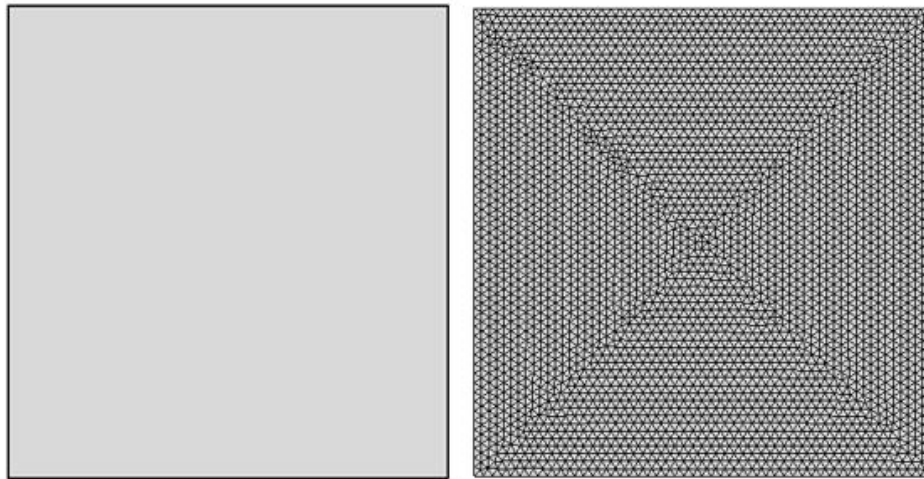


Figure 1. Geometry of Carbon Anode (Left) Meshed Geometry (Right)

2.2. Phase Field model

The initial unbaked baking level at time $t=0$ hours was set as 1. However, the convention of baking level from 1 to 0 could be a bit counter-intuitive. Therefore, at this stage we re-define the baking level (θ) as $1-\phi$ i.e. the BL values is 0 at time $t=0$ hours:

$$\theta = 1 - \phi \quad (5)$$

where: θ Baking level

With this convention, the much more intuitive transition of baking level from a value close to 0 to a value of nearly 1 is established. Also, since the temperature of the complete carbon anode cannot be uniform, a small difference in BL could be present at different locations within the anode. To address this problem, a random function for initial baking level was generated with a mean value of 0.005 and a small tolerance of 0.0005. The random function so developed is shown in Figure 2.

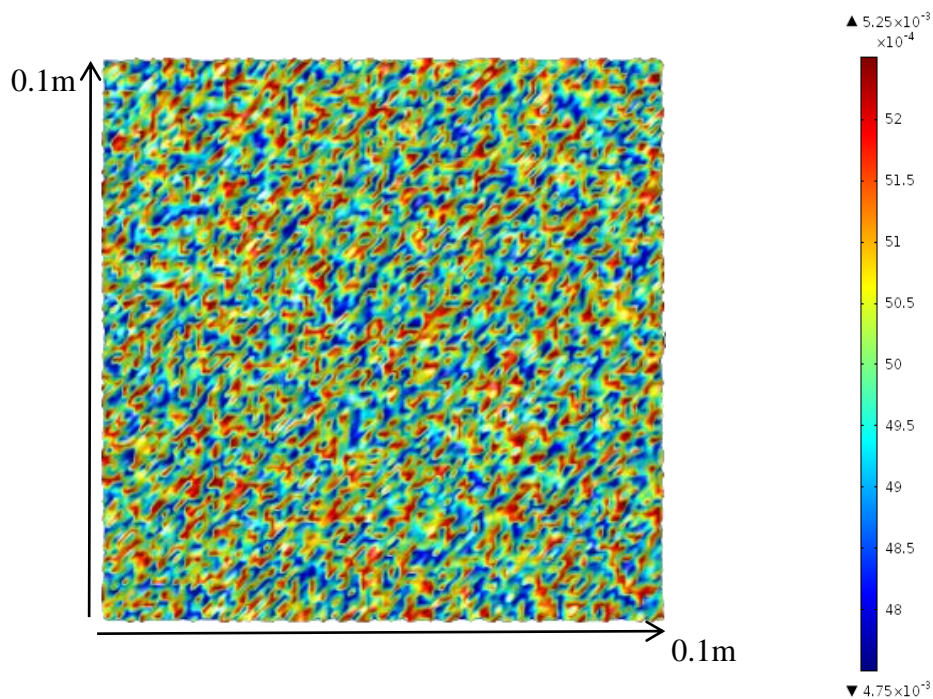


Figure 2. Initial random baking level distribution

The governing equations for the model have already been mentioned in the previous paragraphs. The anode temperature profile was obtained from the work of Tajik et. al [5] using their developed Anode Baking Kiln Analysis (ABKA) software. The time dependent temperature profile being used in the model from ABKA was plotted and is shown in Figure 3. The total time considered for baking process is 132 hours based on three preheating sections (22 hours each) and three firing sections (22 hours each). Partial differential equation (PDE) module of COMSOL [6] was used for solving the PFM equations mentioned previously.

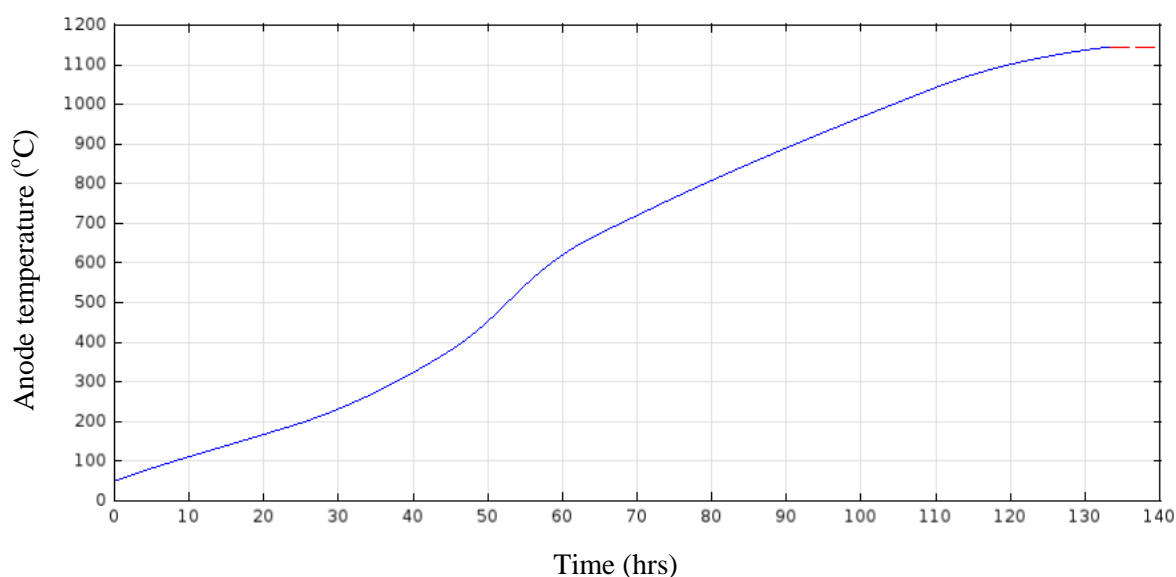


Figure 3. Anode temperature profile

3. Results and discussions

3.1 Evolution of Baking Level

The main purpose of this work is to introduce a PFM based internal state variable i.e. the baking level which is based on thermodynamics and PFT. The contours for evolution of baking level at various time intervals are plotted and shown in Figure 4. It can be seen from Figure 4 that the baking level at a fixed time in the anode may vary for two different points. This is because the temperature distribution within the anode is not homogenous. The historical evolution of average baking level for all times is also plotted in Figure 5. It can be observed that the baking level does not change by appreciable amount during the first 40 hours of the baking process (the first two sections of pre-heating). Soon after 40 hours, the change in baking level becomes more evident as the value approaches to 0.86 by the end of 66 hours. The change in rate of baking level then becomes more pronounced until the baking time reaches 85 hours. After 105 hours, the curve of baking level flattens and approaches a value close to zero which depicts the end of baking process. If the relevant anode temperatures are noticed at these times, at 40 hours the anode temperature reaches a value of 324°C whereas at 85 hours the anode temperature reaches a value of 850°C. It can also be expected that the evolution history of baking level would be sensitive to the applied anode temperature profile, selected values for critical and equilibrium temperatures, and kinetic coefficient in the time-dependent Ginzburg-Landau equation the values of which can all be determined using experiments.

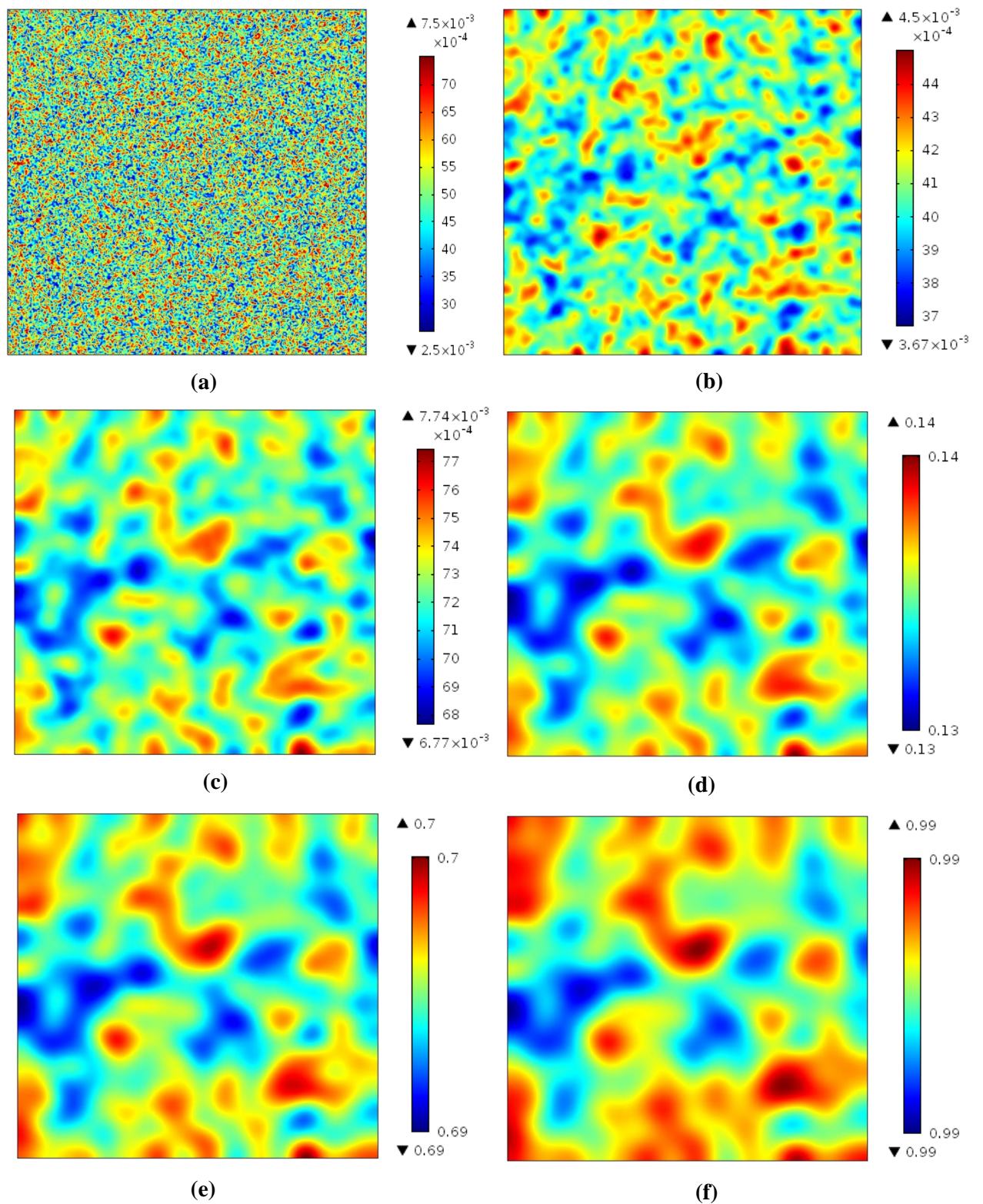


Figure 4. Evolution of Baking Level at different time
 (a) 0 hrs (b) 22 hrs (c) 44 hrs (d) 66 hrs (e) 88 hrs (f) 132 hrs

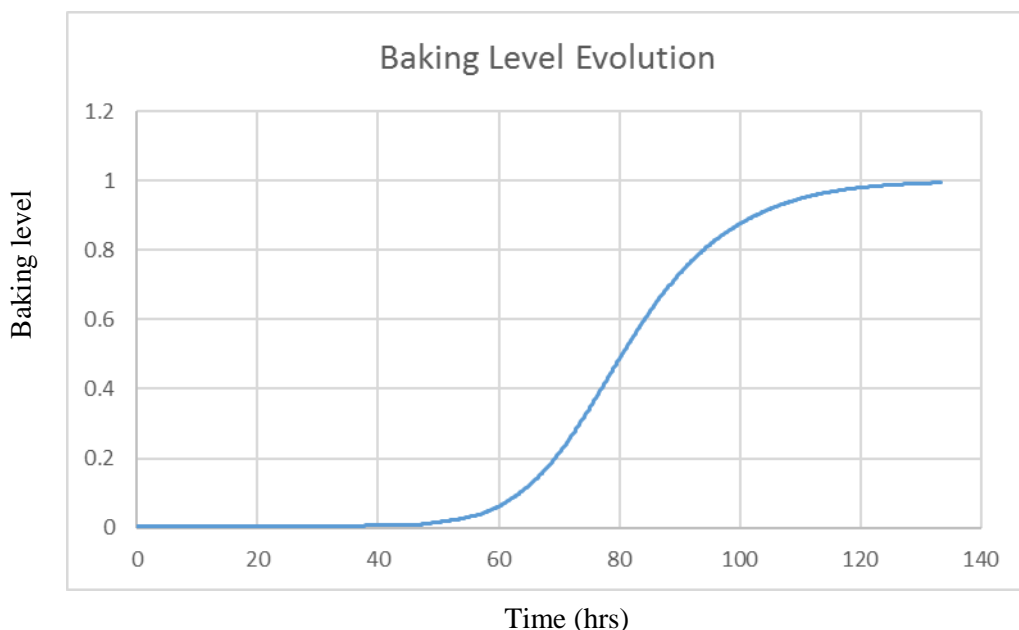


Figure 5. Evolution of Baking Level with time

3.2 Evolution of Anode Material Properties based on Baking Level

An important application of the presented PFT based baking level model could be the prediction of evolution of anode material properties during baking process. Understanding the evolution of baking level during the anode baking process can serve as a pivotal link for establishing the evolution equation for material properties of carbon anode. Though this study does not entirely cover the spectrum of above idea, a scheme for the same will be outlined that can be extended to a comprehensive study in the future. As discussed in the preceding paragraphs, since the baking level has been established on thermodynamics and PFT basis and the fact that the baking process itself is a thermally activated phase transformation, it is quite rational to view the evolution of material properties equation as a function of baking level. Hence, when the baking process is completely defined by its operational parameters, anode temperature profiling can be performed using an advanced computational fluid dynamics (CFD) baking software like ABKA mentioned previously. Based on the anode temperature profile, evolution of baking level can be predicted which in turn would govern the evolution equations for material properties of anode. The formulated equations can later be validated by performing suitable experiments or by comparing with the published data on the subject. The flow chart of the scheme is shown in Figure 6.

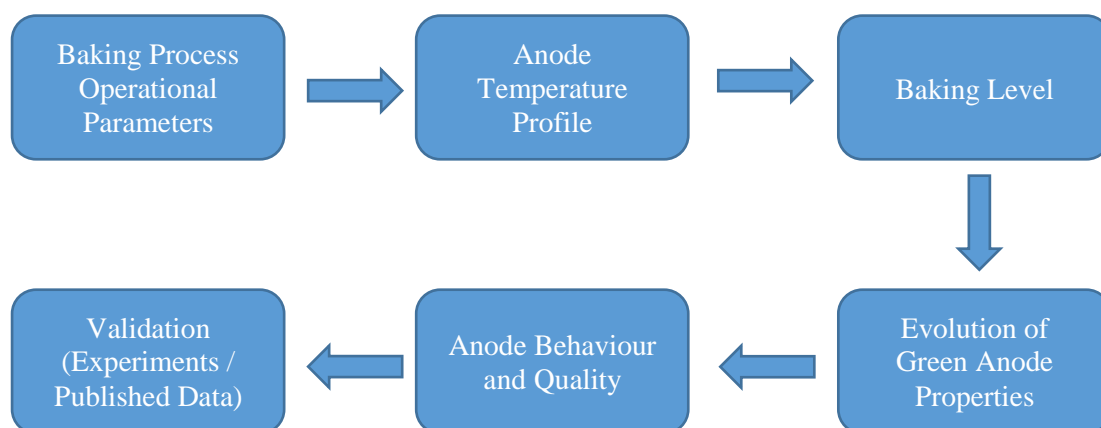


Figure 1. Scheme for Evolution of Material Properties of Anode

During the literature survey, the author discovered that there is a scarcity of published work whether theoretical or experimental on the evolution of green anode material properties during baking process as also mentioned by Amrani et al. [7] Based on the available published sources, the experimental work on evolution of anode properties during baking process presented by Amrani et. al could be referred to as they investigated the evolution of material properties (electrical resistivity, apparent density, internal defects) for scaled down anodes of mass 10 kg manufactured as per the industrial recipe.

4. Conclusions

PFM is a powerful tool that has recently become more matured and richer to address a plethora of varied problems. In this work, an introduction to the utilization of PFM to understand the anode baking process and associated PT of unbaked to baked anode is presented. PFM is an important tool that can be utilized to predict the baking level of carbon anodes at any time during the baking process. In this work, we developed a methodology and computational tool that can predict the baking level at any stage and for any applied anode temperature profile. The PFM so developed could be further refined and calibrated using experimental results that are performed in the conditions analogous to the ones encountered by carbon anode during the baking process. The experimental-based knowledge of variables and parameters required for PFM in the case of anode baking could be helpful to establish strong technical grounds for exploring further areas of application of PFM in the anode baking problem like understanding the evolution of material properties of carbon anode during the baking process.

Acknowledgements

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