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Abstract

The description of the transport mechanisms in operating Li ion battery cells is of key importance for a correct evaluation of their performance and for their optimization.

In this work, we revise the Fickian approach for the description of the lithium transport in intercalation-type active materials. We adopt the Maxwell-Cattaneo-Vernotte (MCV) theory to capture the impact of lithium transport inertia on the electrochemical response of graphitic materials, taken here as an application example. We formalize this theory by means of an analytical mathematical expression which allows extracting the values of the lithium diffusion coefficient D_{MCV} and the inertia characteristic time τ from potentiostatic intermittent titration technique (PITT) experiments. The implications of adopting the MCV theory in single particle models to calculate transient current response during the graphite lithiation are discussed (i) on the basis of the fitting of the calculations with *in house* PITT results and, (ii) by comparing the estimated diffusion coefficients with the ones resulting from the fitting using the classical Fickian approach.

Keywords: single particle model, lithium ion batteries, lithium diffusion, inertia.

Introduction

Lithium ion batteries (LIBs) constitute an energy storage technology intensively used nowadays. The need for electro-mobility based on LIBs starts to be recognized in many countries, due to the global warming and oil depletion issues.[1] This constitutes a significant driving force of many academic and industrial groups carrying out extensive efforts towards the optimization of the LIB electrode materials, electrolyte composition, operating conditions (temperature, C-rate, etc.) and overall cell design for improved energy density, durability, recharge time and safety. A particular mechanism of significant importance in determining the cell operation is the lithium transport in the active materials used in the electrodes. In order to optimize the electrodes, it is important to understand the relationship between the chemical and microstructural properties of the active materials and their associated lithium transport properties.[2, 3] The lithium diffusion coefficient has been used as a relevant descriptor for the comparative analysis of the electrochemical performance of different insertion active materials. Such a diffusion coefficient has been traditionally extracted by fitting mathematical expressions derived from Fick's second law (3), which in turn results from the combination of Fick's first law and the mass conservation equation (Eqs. (1) and (2)). In spherical coordinates we have for the Fick's first law

$$J(r,t) = -D_{Fick}\frac{\partial C(r,t)}{\partial r} \tag{1}$$

whereas the mass conservation equation is written

$$\frac{\partial C(r,t)}{\partial t} = -\frac{1}{r^2}\frac{\partial\, r^2 J(r,t)}{\partial r} \tag{2}$$

which provides

$$\frac{\partial C(r,t)}{\partial t} = \frac{D_{Fick}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C(r,t)}{\partial r}\right) \quad (3)$$

Here J is the diffusive flux, C is the lithium concentration, r is the radial position, t is the time, D_{Fick} is the Fickian lithium diffusion coefficient.

Fick's first law was originally established for the study of chemical species diffusion in biological systems.[4] The diffusion coefficient of LIB active materials is extracted by fitting the calculated potential or current transients to data extracted from experiments using the galvanostatic intermittent titration technique (GITT), the potentiostatic intermittent titration technique (PITT), electrochemical impedance spectroscopy (EIS) or cyclic voltammetry (CV).[5–9]

Wen *et al.*[5] reported the first analytical solution of Fick's second law, in Cartesian coordinates, for the current response under PITT conditions at short and long time scales. The authors represented the electrode as a slab where the lithium intercalation/de-intercalation process was taking place with infinitely fast kinetics (diffusion controlled process). Later, Montella *et al.*[8,10–12] described the current transient for a restricted (blocking) linear diffusion in thin films or foils, or platelet particles in ideal composite electrodes, by neglecting both ohmic potential drop and electrochemical double layer charging effects. Their model introduced "the electrochemical Biot factor" as function of the diffusion, Ohmic and charge transfer resistances. Then, Montella [8] agreed with Deiss,[13] who predicted numerically a spurious potential dependence of diffusion coefficients in insertion electrodes measured with PITT occurring because of the assumption of the infinitely fast kinetics. Then, he proposed a modified Cottrell relationship to consider a restricted (finite-space) diffusion. The modified Cottrell relationship was general regarding the active material geometrical assumptions *i.e.* for the case of linear diffusion, radial diffusion in infinitely long cylinders or diffusion in spherical particles. Li *et al.*[14] developed analytical equations providing the diffusion coefficient and

the interfacial reaction kinetics that allow determining the ratio between the interfacial reaction rate and the diffusion rate. Malifarge *et al.*[15] extracted the diffusion coefficient and the kinetic rate by fitting the experimental PITT current response with a pseudo 2D model based on the porous electrode theory.

Depending on the electrochemical test , the assumed active material particle geometry and the fitting procedure, the extracted lithium diffusion coefficient values may vary very significantly: reported values in literature for graphite are comprised between 10^{-6} and 10^{-11} cm^2/s for the case of graphite.[6,16,17]

The Fickian approach provides a good approximation for most LIB applications involving long discharge at low C-rate. However, for high-power current pulses which can be experienced in automotive or railway applications requiring high C-rate for short times, the Fickian dynamics breaks down because it assumes lithium propagating with infinite velocity. Indeed, the Fick's equation Eq. (3) has a parabolic form which predicts infinite speed of lithium propagation inside the active material while applying a sudden change in the current at the surface of the active material particle (*i.e.* at the active material particle/electrolyte interface). Causality or inertia effect at short time scales is not taken into account, meaning that the lithium flux within the active material particle develops instantaneously with the lithium concentration gradient.[18–20]

For these reasons, a new model is needed to perform accurate prediction and avoid the nonphysical infinite speed. An inertial theory has been proposed by Maxwell, Cattaneo and Vernotte (MCV) [21–23] as a generalization of Fourier law [24–27] for heat transfer. Such a theory has revealed useful for the simulation of thermal waves in solid materials resulting from the application of short laser pulses on their surfaces, and it has been adapted for the case of mass transfer.[28] The associated MCV equation implies that the concentration gradient of a given chemical species at a time t and at a certain position in the material depends on the

molecular flux at the same position and at time $t + \tau$. The relaxation or delay time τ is interpreted to result from the physicochemical interactions of the moving species with their environment. It is worth to point out that the MCV equation is hyperbolic, which prevents the infinite speed propagation ensuring a reliable description of fast transients.

In our work, reported through a series of two consecutive publications, we investigate the implications of the MCV approach concerning the simulation of lithium transport in graphitic materials, at the particle, electrode and cell levels. We use the MCV theory to describe lithium transport in graphitic materials under the effect of short current pulses and we discuss its implications. In this first paper, we obtain from the MCV theory an analytical formulation, then used to extract from PITT experiments the values of the diffusion coefficient and the time delay τ. We analyze the consequences of incorporating the extracted values into a numerical model simulating the electrochemical response of a single graphite particle upon a current step. The paper is organized as follows: first, we present the theoretical derivation, then the adopted experimental techniques and finally we discuss the results and conclude.

Theory

After setting the MCV equation, an analytic solution is derived to extract the values of the lithium diffusion coefficient D_{MCV} and the delay τ, with respect to the initial and boundary conditions for a spherical particle of radius R (Figure 1).

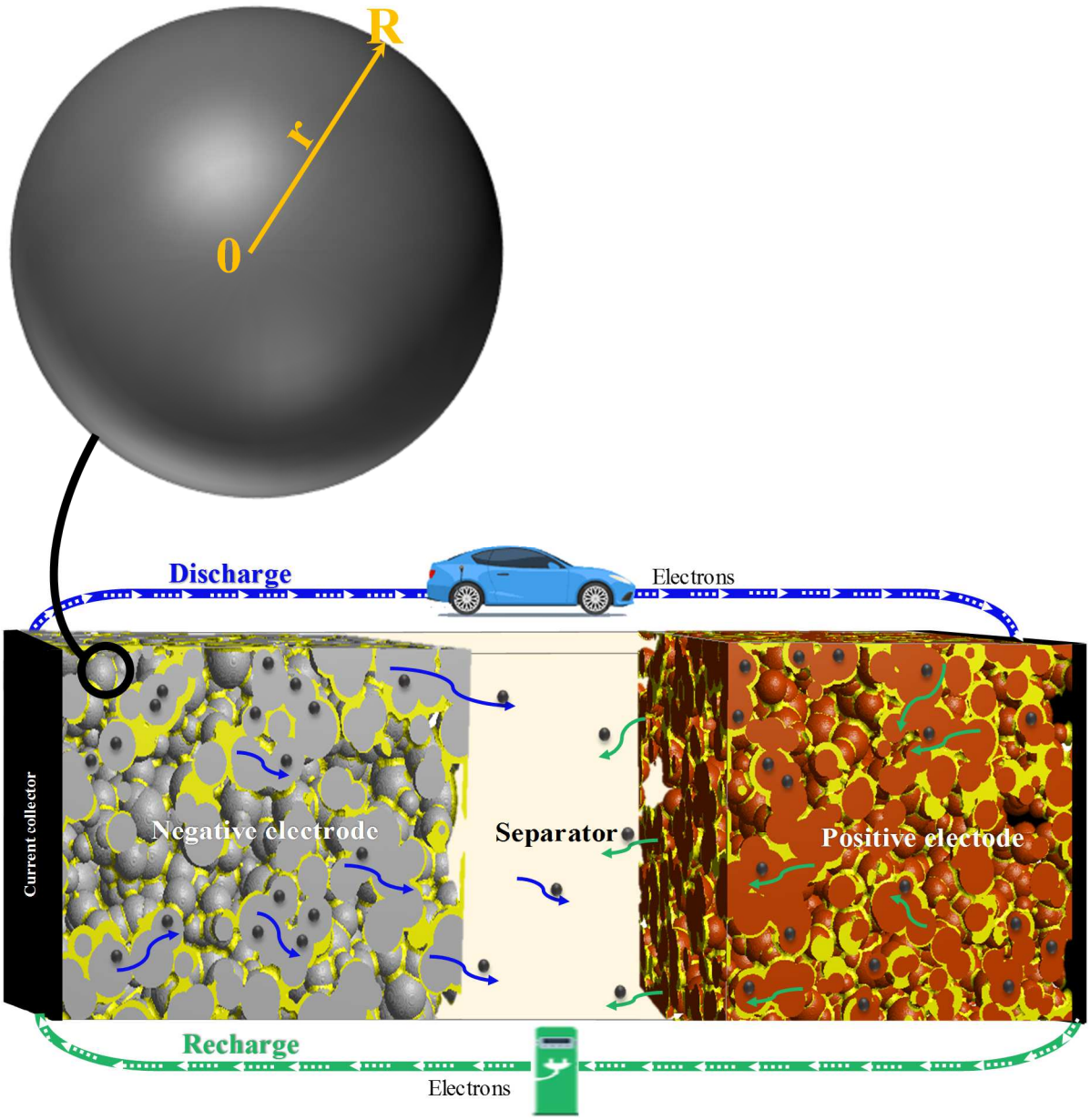


Figure 1. Scheme of a LIB and the graphitic spherical particle being modeled in this work.

Within the MCV approach, the delay τ is added to Fick's first law to take into account the inertia impact in the diffusion process as it follows

$$J(r,t+\tau) \simeq J(r,t) + \tau \frac{\partial J(r,t)}{\partial t} \tag{4}$$

$$= -D_{MCV}\frac{\partial C(r,t)}{\partial r}$$

where a Taylor expansion was applied in the first equality. Combining Eq. (2) with (4) we obtain the following hyperbolic differential equation valid for spherical active material particles of radius R,

$$\frac{\partial C(r,t)}{\partial t} + \tau\frac{\partial^2 C(r,t)}{\partial t^2} = \frac{D_{MCV}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C(r,t)}{\partial r}\right) \tag{5}$$

$$= D_{MCV}\left[\frac{2}{r}\frac{\partial C(r,t)}{\partial r} + \frac{\partial^2 C(r,t)}{\partial r^2}\right]$$

with 0 < r < R.

Equation (5) is solved with the following initial conditions,

$$at\ t = 0\ and\ 0 < r < R, C(r,0) = C_0 = x\ C_s^{max} \tag{6}$$

$$at\ t = 0\ and\ 0 < r < R, \frac{\partial C(r,0)}{\partial t} = 0 \tag{7}$$

By considering an equilibrium state at the graphite particle level at the time just before the current application, the uniform concentration C_0 can be estimated from the state of charge x and the maximal lithium concentration C_s^{max} that can be intercalated in the graphite particle. The boundary condition at the surface of the particle is given by

$$-D_{MCV}\frac{\partial C(R,t)}{\partial r} = -{I(t)}/{_{zFS}}\ , at\ r = R\ and\ t > 0 \tag{8}$$

where F is the Faraday constant, S the surface of the electrode, z the charge number of lithium (equal to 1).

We adopt the method of separation of variables which enabled us to simplify the resolution of the MCV equation into two "independent" equations in terms of variables T and R as it follows:

$$C(r,t) = \sum_{n}^{\infty} C_n(r,t) \quad with \quad C_n(r,t) = R_n(r)T_n(t) \tag{9}$$

Applying first and second temporal and spatial derivatives to $C_n(r, t)$, we obtain

$$\forall n \quad \begin{aligned} \frac{\partial C_n}{\partial t} &= R_n(r)T_n'(t) & \frac{\partial^2 C_n}{\partial t^2} &= R_n(r)T_n''(t) \\ \frac{\partial C_n}{\partial r} &= R_n'(t)T_n(t) & \frac{\partial^2 C_n}{\partial r^2} &= R_n''(t)T_n(t) \end{aligned} \tag{10}$$

Eq. (5) can then be rearranged and divided into two parts, splitting time and space by assuming that both are equal to a negative constant denoted by $-\lambda_n^2$:

$$\frac{T_n'(t)}{T_n(t)} + \tau\frac{T_n''(t)}{T_n(t)} = D_{MCV}\left(\frac{2}{r}\frac{R_n'(r)}{R_n(r)} + \frac{R_n''(r)}{R_n(r)}\right) = -\lambda_n^2 \tag{11}$$

Boundary conditions ensure the constant to be negative by multiplying the second differential equation by $R_n(r)$ and integrating by parts.

The temporal part $T_n(t)$ in Eq. (11) is the solution of the second-order partial differential equation

$$\tau T_n''(t) + T_n'(t) + \lambda_n^2 D_{MCV} T_n(t) = 0 \tag{12}$$

Thus

$$T_n(t) = \exp(\frac{-t}{2\tau})[A_n \exp(-\alpha_n t) + B_n \exp(\alpha_n t)] \tag{13}$$

with

$$\alpha_n = \frac{\sqrt{1 - 4\tau\lambda_n^2 D_{MCV}}}{2\tau} \tag{14}$$

whereas

$$r^2 R_n''(r) + 2r R_n'(r) + \lambda_n^2 r^2 R_n(r) = 0 \tag{15}$$

is solved thanks to the spherical Bessel functions [29] of order 0 to give

$$R_n(r) = j_0(\lambda_n r) = \frac{\sin(\lambda_n r)}{\lambda_n r} \tag{16}$$

After injecting Eqs. (13) and (16) into Eq. (9), the concentration takes the form

$$C(r,t) = \sum_n^{\infty} \exp(\frac{-t}{2\tau})[A_n \exp(-\alpha_n t) + B_n \exp(\alpha_n t)] \frac{\sin(\lambda_n r)}{\lambda_n r} \tag{17}$$

$$C_0 = \sum_n^{\infty} (A_n + B_n) \frac{\sin(\lambda_n r)}{\lambda_n r} \tag{18}$$

We determine the values of λ_n and A_n+B_n by multiplying both sides of Eq. (18) by f_m(r) and by using the orthonormality theorem for series [29]

$$\int_0^R f_m(r)\, C_0 dr = \int_0^R \sum_n^\infty (A_n + B_n) \frac{\sin(\lambda_n r)}{\lambda_n r} dr = \begin{cases} 1 \; if \; m = n \\ 0 \; if \; m \neq n \end{cases} \tag{19}$$

with

$$f_m(r) = \frac{2}{R} \lambda_m r sin(\lambda_m r) \tag{20}$$

Then, it comes

$$if \; m = n, \frac{2}{R} \int_0^R sin^2 \, (\lambda_n r) dr = 1 - \frac{\sin(2\lambda_n R)}{2\lambda_n R} = 1 \tag{21}$$

$$if \; m \neq n, \qquad \frac{2}{R} \frac{\lambda_m}{\lambda_n} \int_0^R \sin(\lambda_m r) \sin(\lambda_n r) \, dr \tag{22}$$

$$= \frac{2}{R} \frac{\lambda_m}{\lambda_n} \left[\frac{\sin\big((\lambda_n - \lambda_m) R\big)}{\lambda_n - \lambda_m} - \frac{\sin\big((\lambda_n + \lambda_m) R\big)}{\lambda_n + \lambda_m} \right] = 0$$

$$\lambda_n = \frac{n\pi}{R} \tag{23}$$

$$A_n + B_n = \frac{2}{R} \int_0^R C_0 \, \lambda_n r sin(\lambda_n r) dr = -(-1)^n 2 C_0 \tag{24}$$

The second initial condition given by Eq.(7), offers the relation between A_n and B_n (Eq. (25)

$$A_n = \frac{\frac{-1}{2\tau} + \alpha_n}{\frac{1}{2\tau} + \alpha_n} B_n \tag{25}$$

Finally, the lithium concentration (Eq. (17)) inside the graphite particle can be expressed as it follows

$$C(r,t) = -2C_0 \exp\left(\frac{-t}{2\tau}\right) \sum_{n}^{\infty} (-1)^n \left[\frac{-1+2\tau\alpha_n}{2\tau\alpha_n} \exp(-\alpha_n t) + \frac{1+2\tau\alpha_n}{2\tau\alpha_n} \exp(\alpha_n t)\right] \frac{\sin(\lambda_n r)}{\lambda_n r} \tag{26}$$

After applying the boundary condition Eq. (8), the current *I* is finally given by:

$$I(t) = \frac{zFSD_{MCV}C_0}{R} \exp\left(\frac{-t}{2\tau}\right) \sum_{n}^{\infty} \left[\frac{-1+2\tau\alpha_n}{2\tau\alpha_n} \exp(-\alpha_n t) + \frac{1+2\tau\alpha_n}{2\tau\alpha_n} \exp(\alpha_n t)\right] \tag{27}$$

with

$$\alpha_n = \frac{\sqrt{R^2 - 4\tau n^2 \pi^2 D_{MCV}}}{2\tau R} \tag{28}$$

Experimental technique

PITT technique is used to investigate the lithium intercalation into the graphite, a material considered in this work as an application example of our theory. Accordingly, an aqueous slurry was prepared, composed of 30% of dry matter containing: 92 wt% SLP30 graphite from (TIMCAL) and 5.3 wt% of carbon black C45 from (TIMCAL) and 2.7 wt% of Carboxymethyl cellulose 3% (Accros). Then it was coated on a copper foil. The average graphite particle diameter was 16 µm and the thickness of the electrode was 30 µm after evaporation and calendering. A coin cell was used to assemble the punched graphite electrode with a diameter

of 11 mm versus lithium metal as counter electrode separated by a glass fiber separator Whatman® (VWR) which was soaked with EC-DMC/$LiPF_6$ (LP30) electrolyte. The coin cell assembly was done inside the glovebox in an Argon atmosphere.

The electrochemical test was performed by charging-discharging the coin cell for 10 cycles between 0.005 V and 1.5 V at C/20 and then a set of potential steps of 5 mV were applied. The following potential step was applied if the current reached a value corresponding to C/500 or the time for the last step exceeded 60 h. The measurement was carried out in a climate chamber using a multichannel potentiostat (VMP-3, BioLogic).

Results and discussion

In this section, we discuss the fitting procedure of the current given by Eq. (27) obtained from the MCV approach with the PITT measurement in the stage transitions during graphite lithiation at rates x close to 0.2, 0.5 and 1. Indeed, it is known that in the plateau regions, the diffusion coefficient cannot be evaluated in contrast to the stage transitions related to single diffusional processes.

The Matlab solver lsqnonlin is used to fit the PITT current response using Eq.(27) by minimizing the following cost function:

$$F = \frac{\left(I^{exp}(t) - I(t)\right)^2}{I^{exp}(t)^2}$$

where I^{exp} is the experimentally-measured PITT current and I is the calculated current.

Figure 2 presents the fitting for one PITT current response following the applied potential step at x = 0.2, achieved with a good precision equivalent to 10^{-4} of order of magnitude.

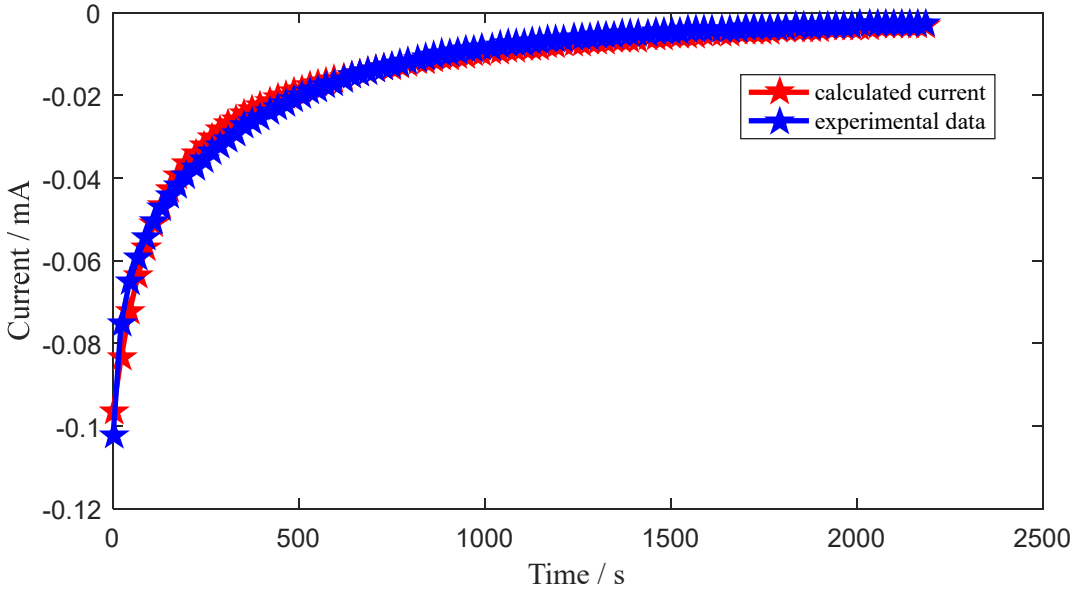
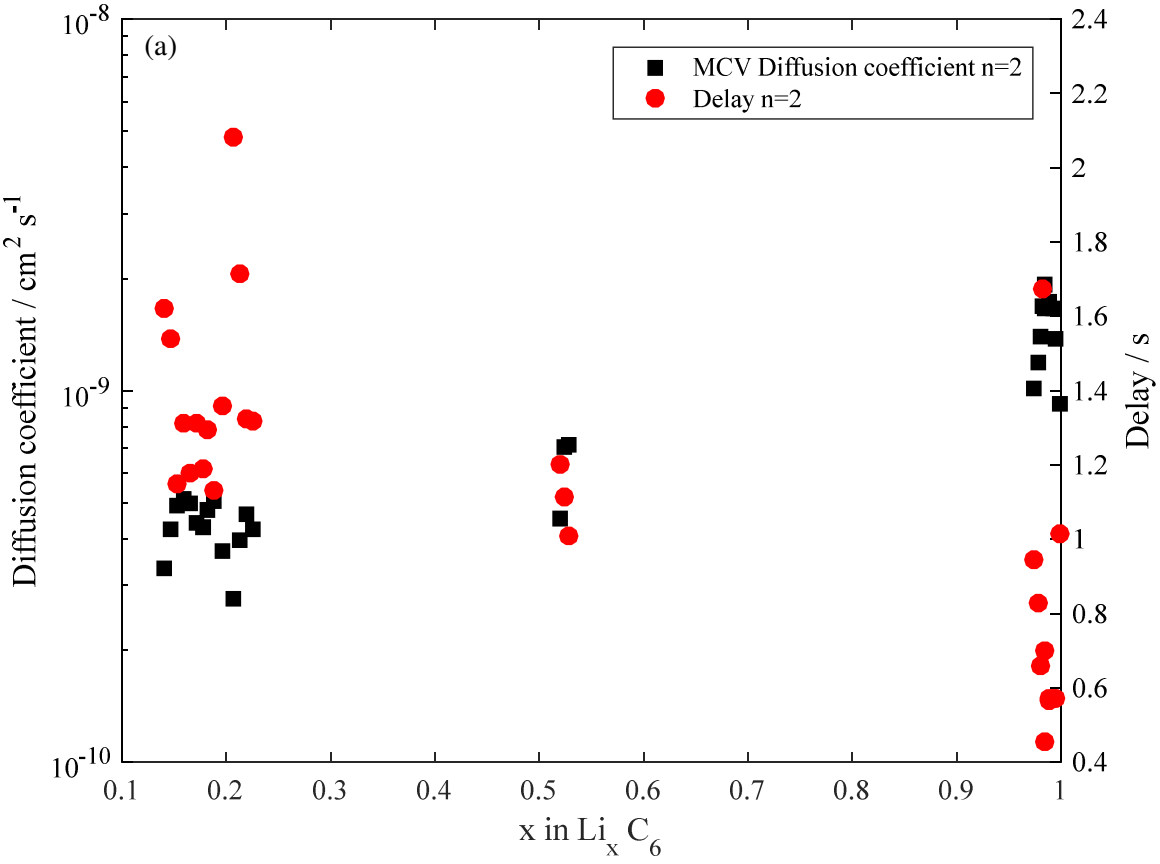
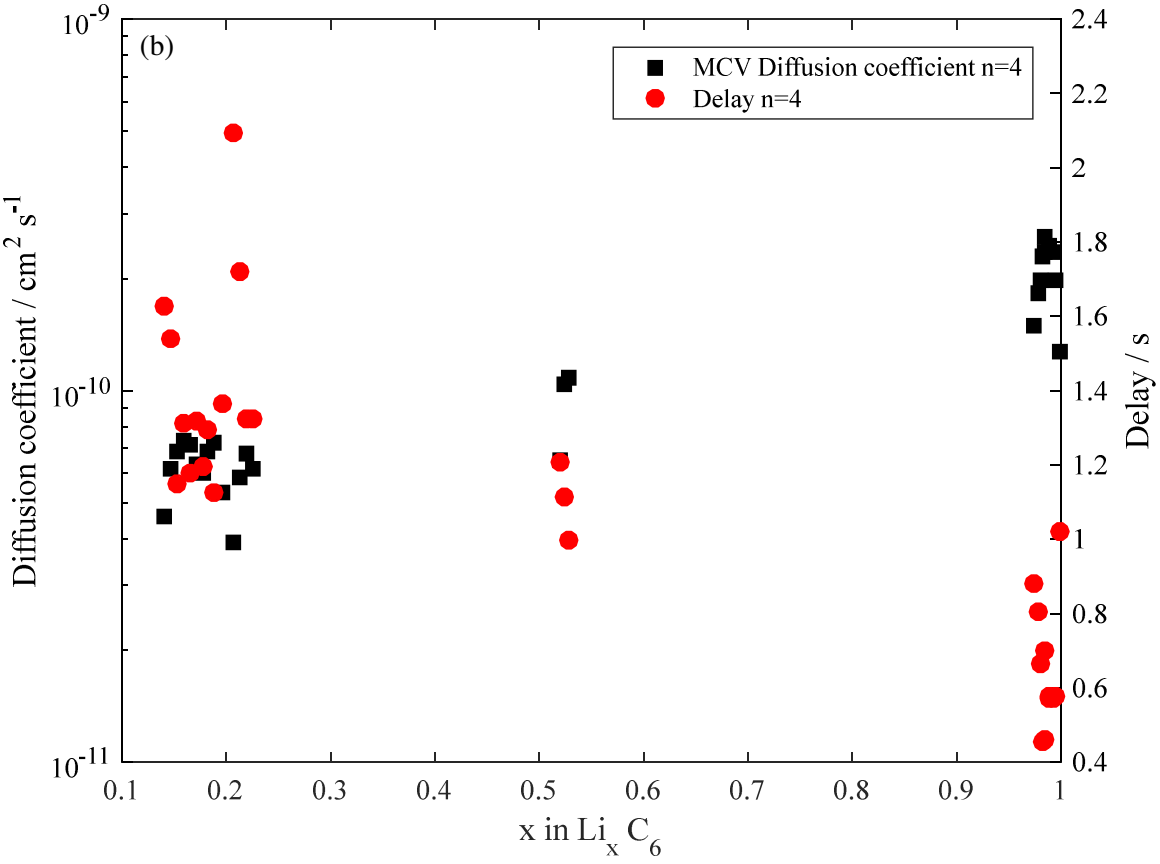


Figure 2. Fitted (red) and experimental PITT (blue) current responses with respect to time following the potential application at x = 0.2.

The fitted values of lithium diffusion coefficient D_{MCV} and delay τ are 2.7 10^{-10} cm^2 s^{-1} and 1.15 s, respectively. The evolution of the diffusion coefficient and the delay are tracked over all the electrochemical response in the solid solution regimes for the series in Eq. (27) accounting n terms with n = 2, 4, 8 (Figure 3).


(a)
MCV Diffusion coefficient n=2
Delay n=2
Diffusion coefficient / cm^2 s^{-1}
Delay / s
x in Li$_x$ C$_6$
10^{-8}
10^{-9}
10^{-10}
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4


(b)
MCV Diffusion coefficient n=4
Delay n=4
Diffusion coefficient / cm 2 s-1
Delay / s
x in Li x C 6
10-9
10-10
10-11
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4

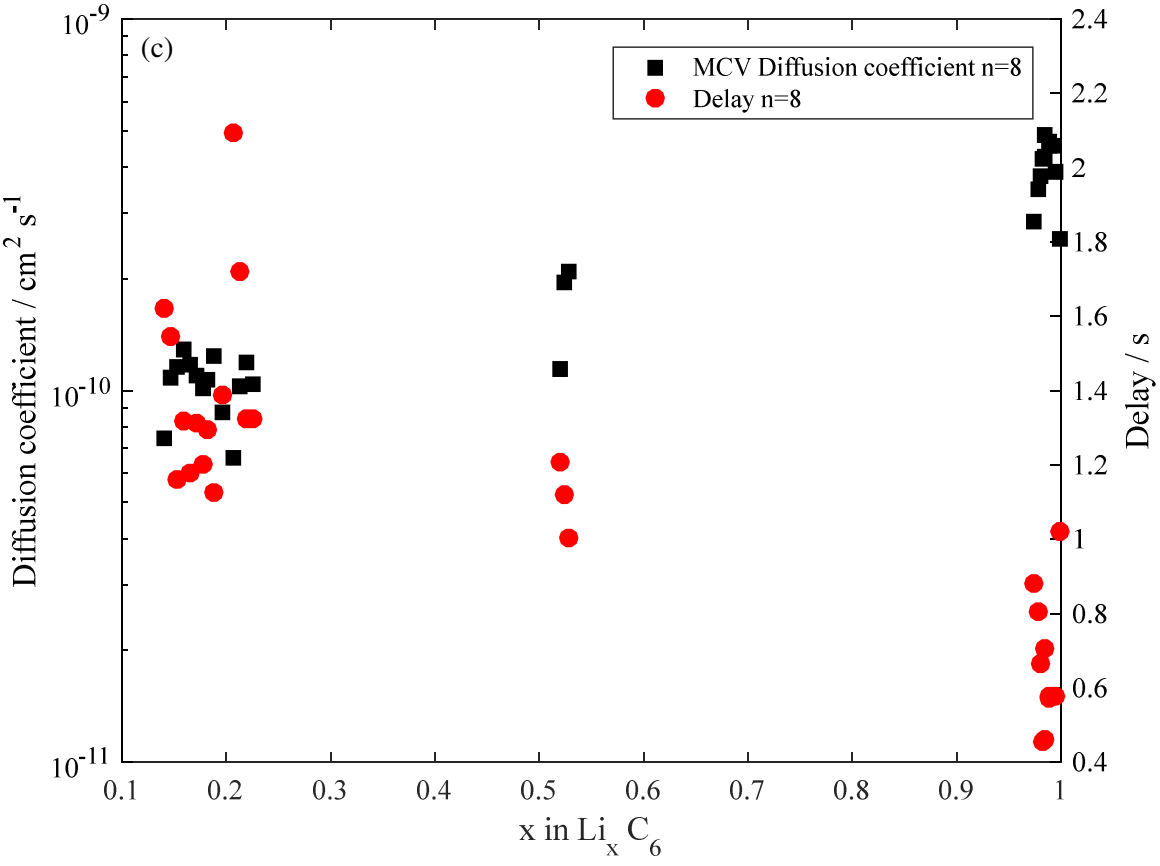

(c)
MCV Diffusion coefficient n=8
Delay n=8
Diffusion coefficient / cm 2 s-1
Delay / s
x in Li x C 6
10-9
10-10
10-11
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4

Figure 3. Calculated diffusion coefficient D_{MCV} (in black) and the delay τ (in red) as function of the lithium insertion rate x for different number of terms in Eq. [27], n = 2 (a), n=4 (b), n=8 (c).

It is clearly observed that the diffusion coefficient preserves the magnitude order almost the same order of magnitude for each state of charge during lithium intercalation, which would mean that we get closer to the intrinsic properties of the material. We also notice an increase of D_{MCV} values together with a decrease of τ values with the insertion rate x.

The delay τ quantifies the time needed for lithium to have access to another site inside the graphite particle. This delay can result from the physicochemical interactions of the moving lithium with its local environment within the graphite material. There may be a competition between C-C weak van der Waals (vdW) bonds between the graphene sheets, which decreases, and the Li-C bonds, which increases upon lithiation.[30] The lithium fits reversibly into vacant interstitial sites until it reaches the saturated stage 1 to form the LiC_6 compound. During the potential disturbance application, the inserted lithium moves to other sites leaving place to other inner lithium in a continuous way until the flux becomes zero and the equilibrium is established. The hopping mechanism from one site to another at the particle level has been already investigated in literature with different theoretical models following Fickian dynamics.[30–32] We believe that the MCV equation presents an alternative approach linking the lithium intercalation into the graphite particle at the atomistic scale with mass transport characteristics at the macroscopic level.

The impact of the number of terms n considered in the Eq. (27) is investigated to evaluate the criteria of convergence for the solution (Figure 4). The current can be calculated with good precision with a residual of 10^{-4} for n=4.

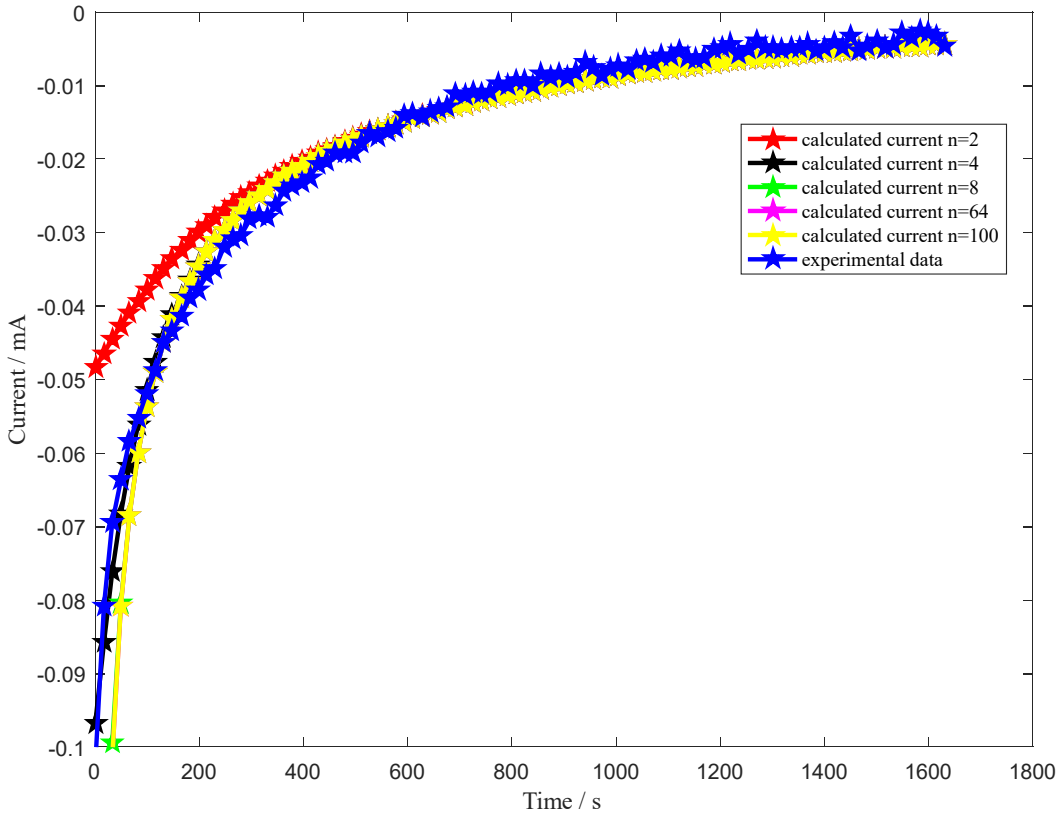


Figure 4. Convergence with respect to n of the calculated current calculated from the analytical model by using fitted parameters (D_{MCV}, τ) with the experimental data during the first transition at 0.186 V.

Figure 5 displays a comparison of diffusion coefficient values extracted with both the MCV and Fickian approaches. The Fick's diffusion coefficient D_{Fick} is calculated according to the modified Cottrell relationship provided by Montella for spherical particles.[8] The value D_{Fick} is higher by three orders of magnitude during the first transition phase, by two orders of

magnitude during the second transition and similar in the lithiated stage that the D_{MCV} which does not present such remarkable variation.

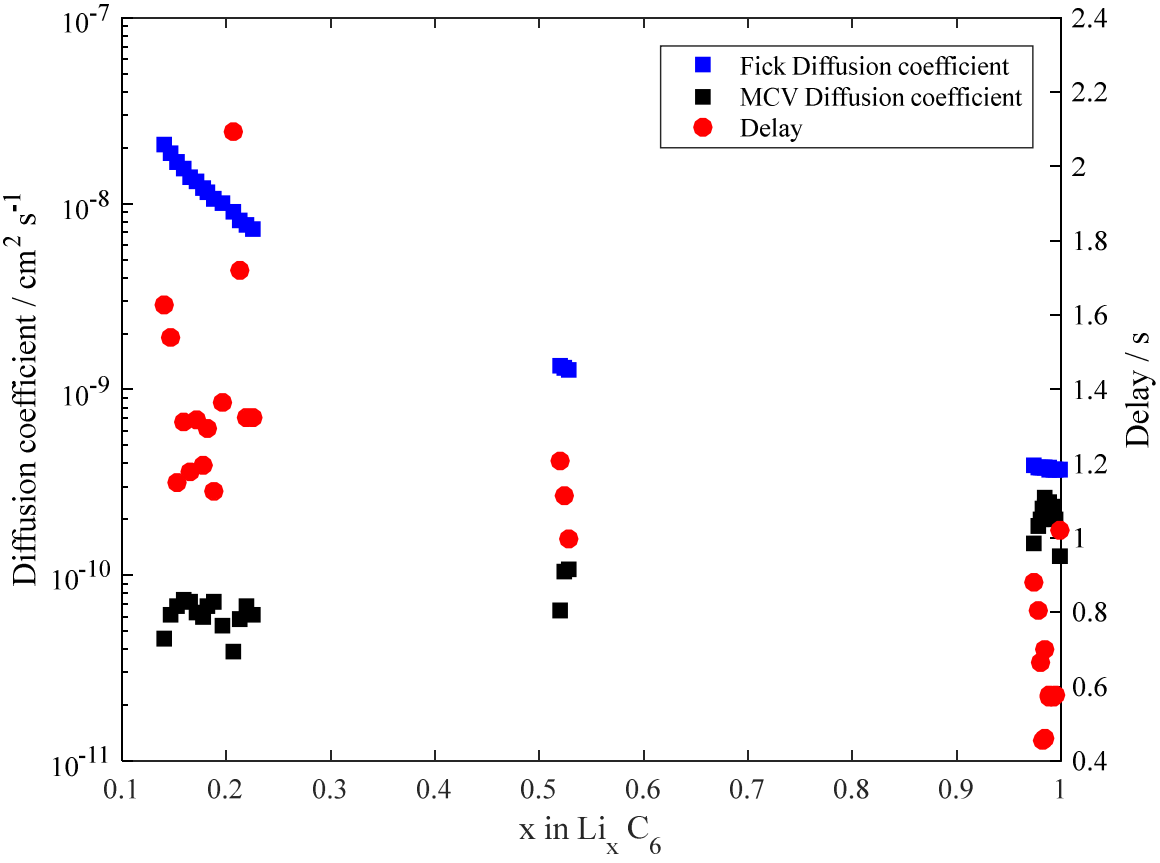


Figure 5. The calculated evolution of the MCV and Fick's diffusion coefficients D_{MCV} (in black), D_{Fick} (in blue) and the delay τ (in red).

In the fitting procedure we calculate the gradient of the strictly convex function (that implies the existence and uniqueness of the minimum) $F = \frac{\left(I^{exp}(t) - I(t)\right)^2}{I^{exp}(t)^2}$. To simplify for the MCV case, let us consider the zeroth order series $I(t) \simeq D_{MCV} exp\left(\frac{-t}{2\tau}\right)$. Then, knowing

experimentally-measured PITT current at two different times t_1 and t_2, a direct computation gives $D = I_1^{exp} exp\left(\frac{t_1}{2\tau}\right)$ and $\tau = \frac{t_1 - t_2}{2\left(lnI_1^{exp} - lnI_2^{exp}\right)}$. From those equations, it is clear that the observed variations in the fitted quantities are strongly related to the current dynamics from case to case. It is also clear from these equations that, on the one hand, D increases when τ decreases. On the other hand, larger is the current variation between two consecutive times, smaller is τ.. This behavior is not obvious and the observed trends with MCV indicate that the lithium transport process in the active material may be much more complex that what is assumed in the Fickian's approach. For instance, such a transport can offer wavy behavior, inherently described by the MCV theory. Such a wavy behavior has been already observed by using phase field modeling approaches.[18,34]

It is difficult to advance why the Fick diffusion coefficients are larger than the ones obtained with the MCV theory (besides some argument related to the fact that Fick's approach inherently considers an infinite propagation speed of lithium), but we can affirm that our fitting procedure is optimized and that the fitted data is correct. Indeed, concerning the full series, a set of initial conditions has been used to avoid convergence in our fitting procedure to a local minimum.

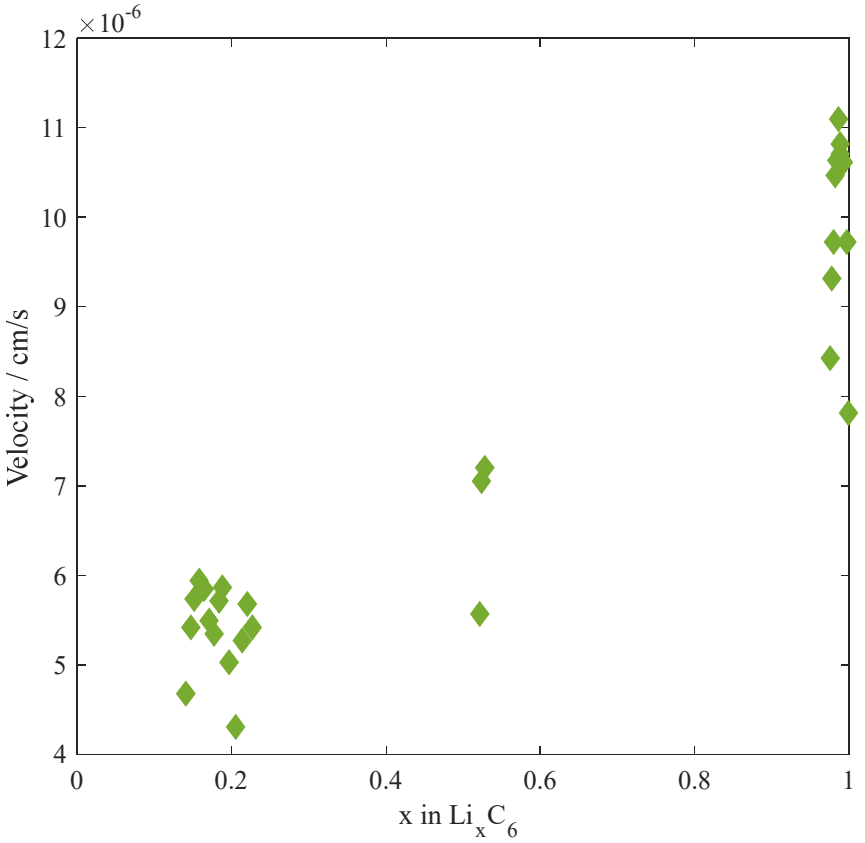
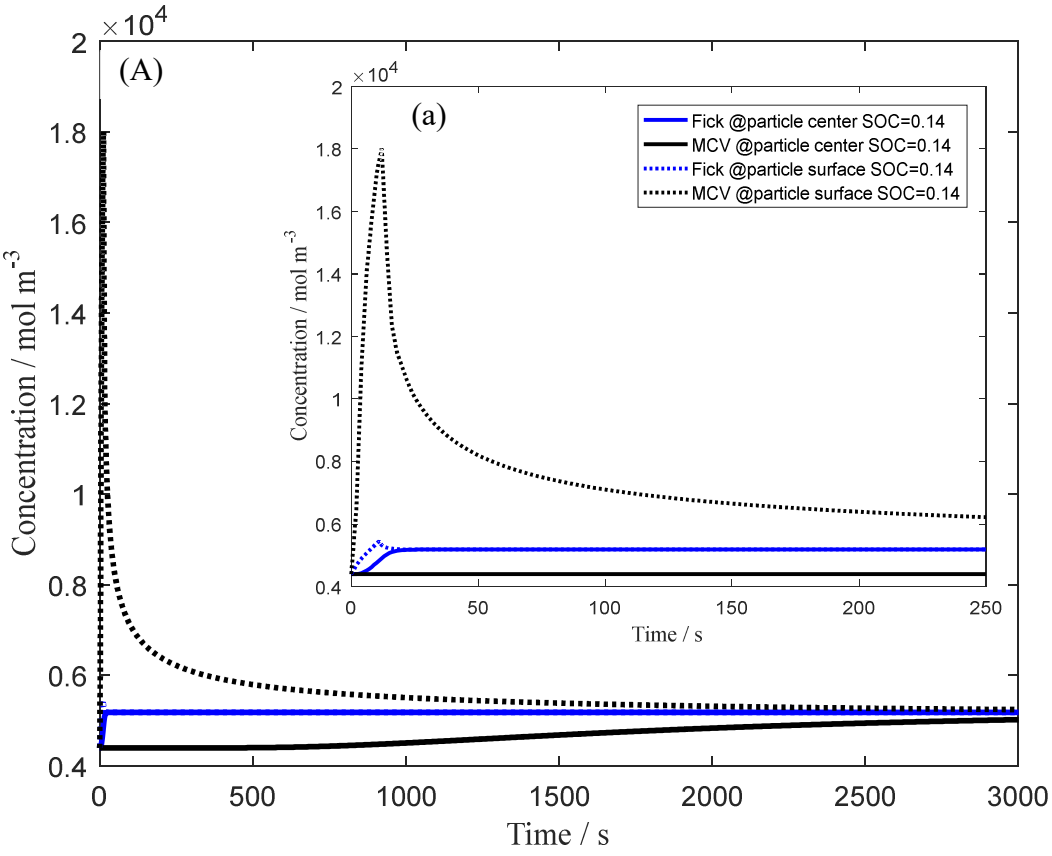


Figure 6. Calculated velocities during lithium insertion as function of x.

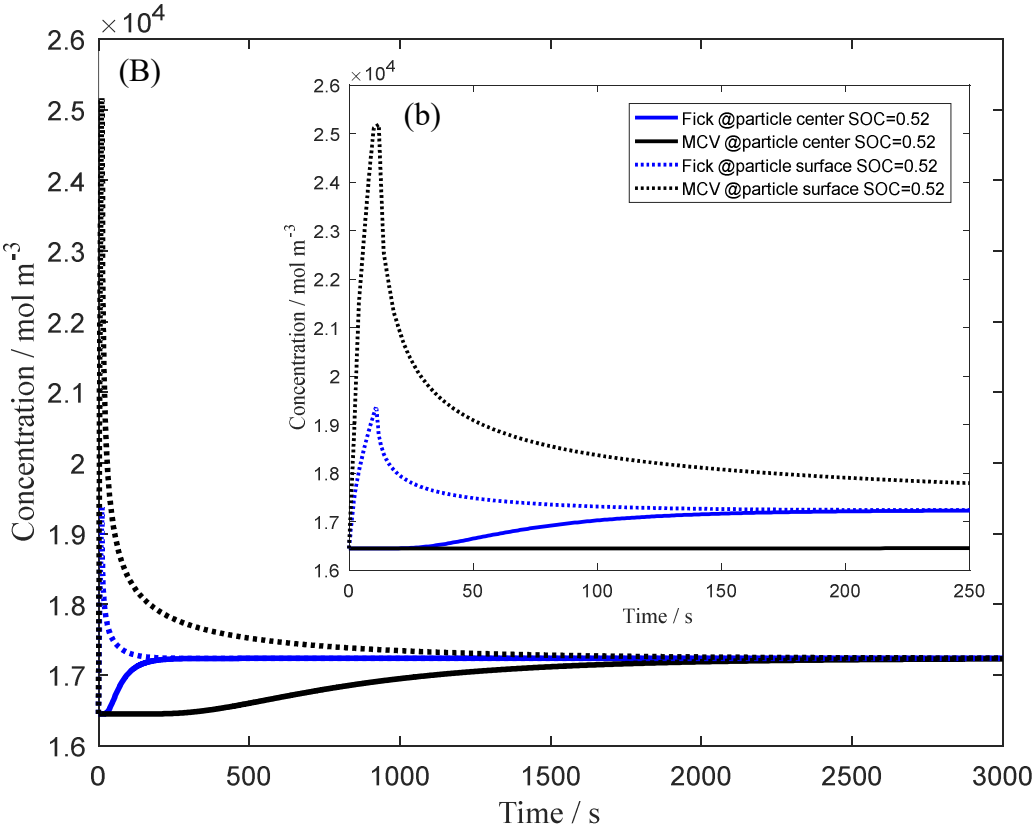
Figure 6 presents the calculated evolution of the lithium front propagation speed inside the graphite active material particle (velocity $=\sqrt{D_{MCV}/\tau}$, by analogy of the MCV equation with the Telegraph equation [23]), which is observed to increase with *x*. We note that more we get closer to the fully lithiated state, faster is the filling of the remaining unoccupied graphite sites, as it becomes easier to the inserting lithium to reach its final location as it has less possibilities to microscopically interact with its environment within the graphite particle.

The resulting values D_{Fick}, D_{MCV} and τ are implemented in a numerical single particle model subject to the application of a current pulse applied to its surface and equivalent to 10 C (here C is equivalent to 1.13 mAh) during 10 s. The simulations are performed by solving Eqs. ((3) and (5). Figure 7 displays the lithium concentration calculated with Fick's and MCV approaches

at both particle center and surface for three states of charge (SOC) corresponding to the phase transition during graphite lithiation. The concentration modeled with Fick's equation reaches earlier the relaxation state than the one simulated with MCV (Figure 7 a, b, c): this illustrates the effect of the infinite propagation speed of lithium inherent to the Fick's first law and leading to the instantaneous lithium distribution everywhere inside the particle. However, it is obvious that in the case of MCV there is a lag in the concentration evolution at different radial positions *r*. The particle center remains at its initial concentration for a while, until the lithium front arrives to the center of the particle from the surface. It is also highlighted that at long time scale, the concentration becomes the same everywhere in the particle with both approaches (Figure 7 A, B, C). Front propagations, as captured with the MCV theory, may lead to active material particle microstructure damage under high rate short-pulse cycling conditions.


(A)
(a)
Fick @particle center SOC=0.14
MCV @particle center SOC=0.14
Fick @particle surface SOC=0.14
MCV @particle surface SOC=0.14
Concentration / mol m-3
Time / s

]


(B)
(b)
Fick @particle center SOC=0.52
MCV @particle center SOC=0.52
Fick @particle surface SOC=0.52
MCV @particle surface SOC=0.52
Concentration / mol m-3
Time / s

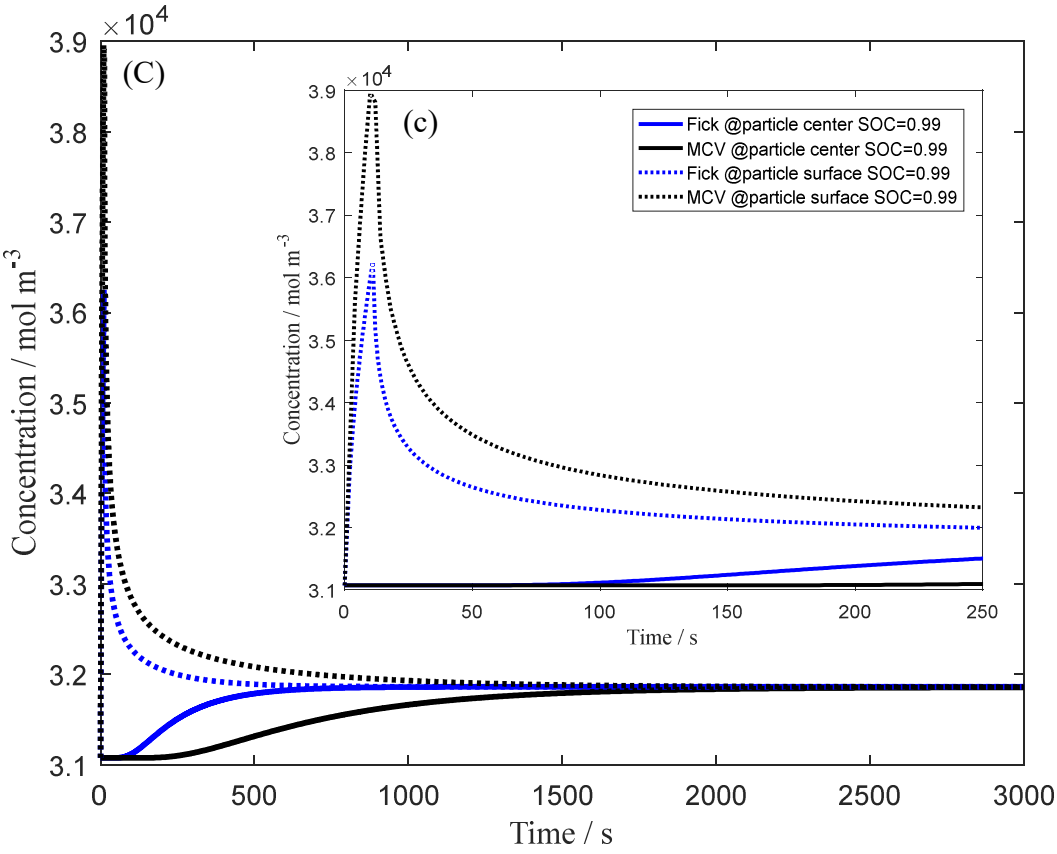


Figure 7. Lithium concentration profiles simulated with Fick's (blue) and MCV (black) approaches at both particle center (continuous line) and surface (dashed line) for three states of charge *SOC*= 0.14(A, a), 0.52(B, b), 0.99 (C, c).

Conclusions

In this work we adopt the Maxwell-Cattaneo-Vernotte (MCV) theory to capture the impact of lithium transport inertia on the electrochemical response of LIB single particle models, by considering the graphite active material as an application case. We evaluate the implications of this theory in comparison to the classical Fickian approach. The comparison between both approaches allows providing an interpretation of some observed electrochemical behavior and can help in deciding on the most appropriate physical description to adopt for each specific LIB

application condition. An analytical solution of the MCV equation offers a tool to fit each potential step in PITT experiments and to extract the MCV diffusion coefficient D_{MCV} and delay τ simultaneously during the graphite lithiation. The present procedure shows versatility to capture the impact of inertia on the electrochemical response for power applications requiring high C-rate for short times where some seconds are decisive for the performance of LIB in real time. We believe that the reported work is of interest for deepening the understanding on the lithium transport mechanism in LIB active materials.

We underline that the impact on the electrochemical response of the time delay τ introduced by the MCV theory is to be distinguished from other possible transient effects, such as the one originated by the active material/electrolyte interfacial double layer charging/discharging upon LIB cycling.[33] In the future, we plan to work on electrochemical cycling test with optical observations for a graphite single particle as a tool for lithium diffusion coefficient and delay experimental extraction. In a second consecutive publication, we investigate the implications of the integration of the MCV theory and extracted parameters into a graphite *vs.* Li cell model in regards of the prediction of its electrochemical performance [35].

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Abbreviations

J	diffusive flux, mol/m^{2}s
D_{Fick}	diffusion coefficient from Fick's law, cm^2/s
D_{MCV}	diffusion coefficient from MCV approach, cm^2/s
τ	delay, s
t	time, s
r	radial position in the particle, cm
R	particle radius, cm
I	current response, mA
S	geometric surface area, cm^2
z	charge number of lithium

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