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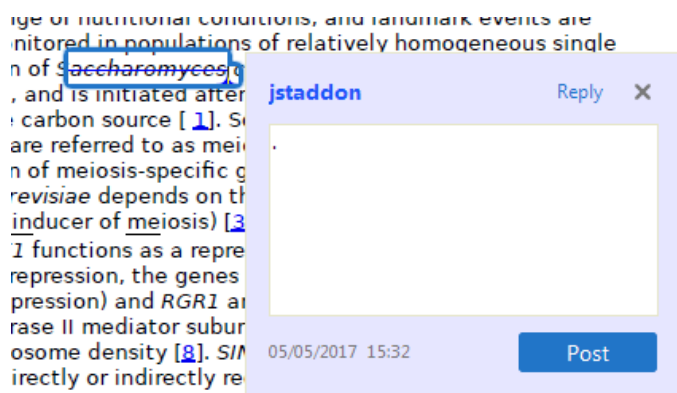




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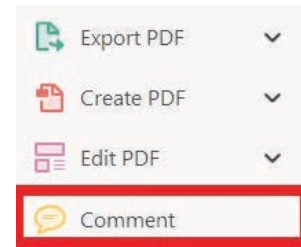
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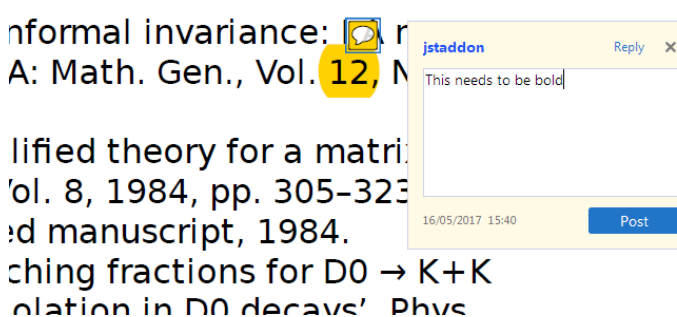
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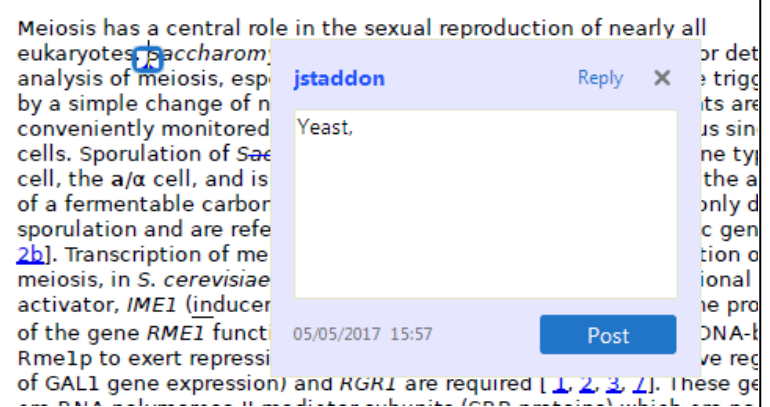
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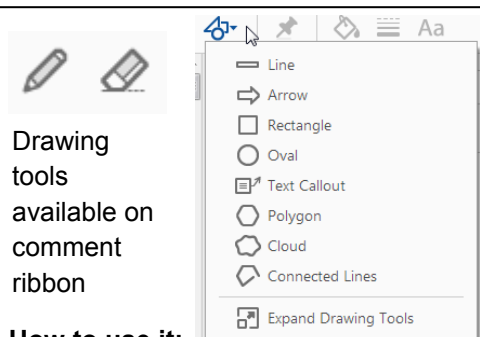
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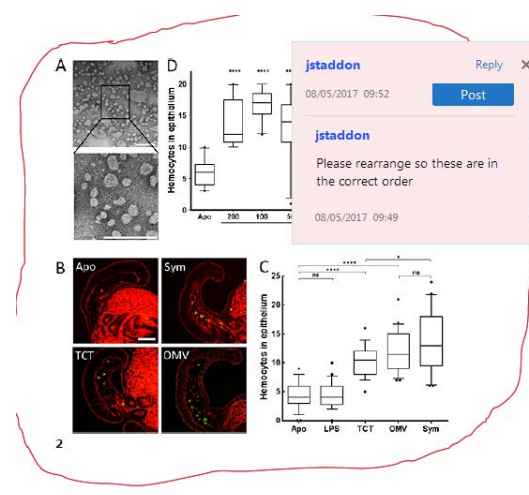
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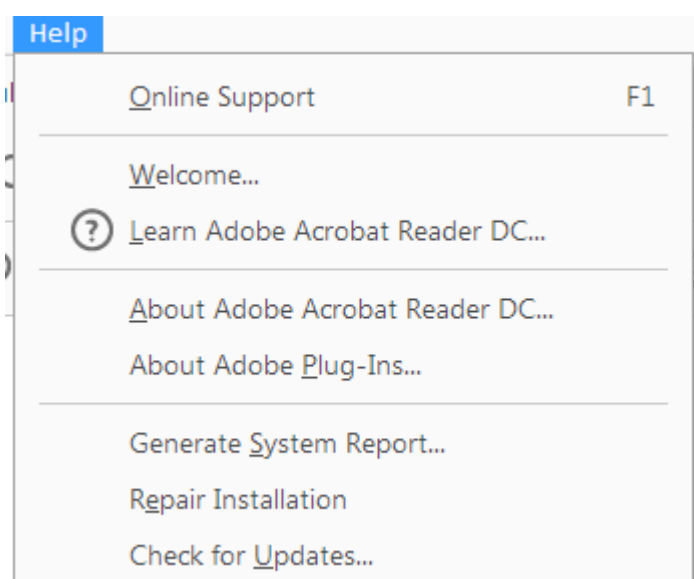
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# Model Based Analysis of Lithium Batteries Considering Particle-Size Distribution

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*Performance of lithium ion batteries whose electrodes are composed of particles of different sizes is studied. Simplified model developed in (Henquín and Aguirre, AIChE J. 2015; 61:90–102) is extended and the simulations are compared with experiments from the literature so as to validate this new model. The differences in current density observed in particles of different sizes, which are in contact, depend on particle size and state of charge. Internal particle to particle discharge currents are observed during relaxation times. A parametric study of the applied current and particle sizes of electrodes is performed to evaluate cell performance, with emphasis on cell voltage and final capacity measurement. The evolution of reaction rates on the surface of electrode particles and their corresponding states of charge are depicted. An analysis of relaxation times in terms of cell voltage, current density, equilibrium potentials, and overpotentials is included.* © 2017 American Institute of Chemical Engineers *AIChE J*, 00: 000–000, 2017
*Keywords: lithium ion batteries, different particle size, simplified mathematical modeling*

## Introduction

High power lithium batteries manufacturing and use for mobile applications (such as cars), or stationary (energy storage in homes and public buildings) have become very promising due to their multiple advantages.[1] The market of high energy density and power storage batteries is constantly expanding.[2] However, for the proper operation of these units, a very thorough control of the variables involved in charge and discharge processes must be taken. Therefore, it is necessary to count on phenomenological and predictive mathematical models (rigorous but simple to interpret and solve) that are capable of predicting the phenomena produced in batteries. Thus, Doyle et al.[3] developed a novel theoretical model for uniform particle size batteries which was corroborated by experimental points at charge and discharge of two different batteries. However the predictive capacity of this model strongly depends on ad hoc parameters to achieve the adjustments with experimental results, as recognized by the authors themselves, as they frequently have to resort to correlative parameters to achieve the adjustments with experimental data points. The model also has several coupled Partial Differential Algebraic Equations to be resolved. Thus, with the aim of facilitating resolution and reducing calculation times,

a series of model reformulations[3] are presented in Ref. 4. Other authors have worked on simplified mathematical models that are analogous to electric circuits,[5,6] thus obtaining very fast models involving lesser phenomenological predictive capacity compared to the previously mentioned. In a previous paper,[7] we presented a simplified mathematical model, based on mass and energy balance equations. The main advantages of our model compared with other models mentioned above are that (i) currents balances are used correctly and properly (Eq. 6), which are integral equations instead as local one as is the case in the original work[3] (ii) a theoretical based equation for the conductivity of electrolyte (Eq. 10) is used, with better adjustments to the experimental points compared to the original work, as shown in Figure 2 (iii) the model results in a set of ordinary differential and algebraic equations, very simple to solve (iv) no parametric adjustments as contact resistance are necessary (v) the model can be reduced to a simpler entirely algebraic system, which also fits with the experimental points. In summary the model is highly predictive and simple enough to be solved even in spreadsheet calculations.

To achieve simple mathematical models and rapid resolution, some authors sacrifice predictive power, despising certain phenomena or including strong simplifications. In facilities where the use of large banks of lithium batteries is required, it is not convenient to take extreme simplifications in mathematical models because high-capacity batteries are used in cycles and are subjected to different charge and discharge rates. In this sense, many authors have shown a growing interest in developing mathematical models, focusing their attention on

the phenomena produced in electrode particles. Thus, in Ref. 9, a model considering a single particle is developed by Zhang et al. The results of three models of different complexities are compared in Ref. 4. An early work describing a pseudo 2D model that includes diffusion inside particles, diffusion in electrolyte phase, and that incorporates Butler-Volmer kinetics was performed by Doyle et al.[10]

The need for mathematical models to predict the phenomena occurring inside batteries becomes evident, taking into account particle-size distribution on electrodes. An extensive review of mathematical models considering the number of particles in electrodes was performed in Ref. 11. Experimental work with X-ray studying the effect of electrode microstructure of batteries was performed in Ref. 12. In Ref. 13, the amount of Li+ ion intercalated in natural carbon flakes whose particle size ranges from 2 to 40 $\mu$m was experimentally studied. In others studies,[14–23] the close relationship between particle size and electrode morphology, among other variables, was confirmed for battery performance. In Ref. 14, the improvement of the electrochemical properties of particles by decreasing particle size was suggested. A mathematical model describing the effect of electrode microstructure on galvanostatic discharge was performed in Ref. 17. The finite element method was used, and solid-electrolyte interface potential, equilibrium potential, and ohmic drop were related. In Ref. 21, self-discharge rate is related to electrode particle size and electrode surface area. The authors of Ref. 22 focus their attention on conductive additives and the distinction between primary particle, aggregate, and agglomerate.

Conversely, the performance of large storage systems can be affected by the use of an improper technique for selecting particle size. Thus, in Ref. 23 the effect of particle size and electrode thickness on the reaction rate is studied. A mathematical model and experiments are presented by the authors of Ref. 24. They use an empirical expression that takes into account the number of contacts between solid particles and the average contact resistance. In addition to calculating transport properties, a discretization of the actual particle-size distribution is used

In Ref. 25, the effect of particle size and speed of cycling, among other variables, on the specific energy of batteries is theoretically addressed. This issue has attracted the attention of authors who attempted to study the consequences of this problem in large units. So, Kenney et al.[26] extended the single particle model to study a system of batteries—used to supply power for a home—which had slight variations in electrode manufacturing. In Ref. 27, the problem of coexistence of different particle sizes is also shown. Darling and Newman developed a mathematical model based on,[10] which was applied to a cell whose positive electrode is $Li_yMn_2O_4$, and its negative is a lithium foil. The work studies the influence of considering two different particle sizes on the states of charge in cycles, temporary cell voltage responses, and relaxation times. Unfortunately, and as it was mentioned in Ref. 7, these models have multiple differential equations coupled with their contour conditions.

Lithium Iron-Phosphate batteries are studied in Ref. 28, emphasizing the existence of diffusion areas in the solid phase. In the same way, the authors propose the model with two-size electrode particles, but considering the same surface area and volume fraction as those of a single-size particle battery. The authors of Ref. 29 emphasize the idea of diffusion directions in the solid phase and the idea of incorporating a distribution of particle sizes to describe battery behavior.

Based on the study of these bibliographies, it is demonstrated the importance of simplified mathematical modeling, and the interest in studying the impact of particle-size distribution in the electrodes on the performance of the battery. Hence, in this article, the mathematical model presented in Ref. 7 is extended and adapted to calculate cell voltage, reaction rates, states of charge, equilibrium potentials, and other ohmic drops inside the battery, considering that electrodes are composed by particles of two different sizes. The model is validated by comparing theoretical predictions with experimental points of two batteries using different electrode materials. A parametric study of battery variables is performed with the aim of studying the temporal response to different discharge conditions and considering different particle sizes. Internal currents inside the battery along relaxation processes are computed.

## Theoretical Considerations

As previously stated, the mathematical model being used has its bases published in Ref. 7 and is adjusted to a system of more than one particle. Thus, the salt balance in the electrolyte is

$$\frac{dC_e^A}{dt} = \sum_m j_m^A \left(1 - t_+^o\right) \frac{a_{e/s,m}^A}{v_e^A} \, n_m - K_1^A \left(C_e^A - C_e^S\right) \frac{a_{tr.e}^A}{v_e^A} \quad (1)$$

$$\frac{dC_e^C}{dt} = \sum_m - j_m^C \left(1 - t_+^o\right) \frac{a_{e/s,m}^C}{v_e^C} \, n_m + K_1^C \left(C_e^S - C_e^C\right) \frac{a_{tr.e}^C}{v_e^C} \quad (2)$$

$$\frac{dC_e^S}{dt} = K_1^A \left(C_e^A - C_e^S\right) \frac{a_{tr.e}^A}{v_e^S} - K_1^C \left(C_e^S - C_e^C\right) \frac{a_{tr.e}^C}{v_e^S} \quad (3)$$

where $K_1^A$ and $K_1^C$ can be considered as a global mass-transfer coefficient between anode and separator and separator and cathode; and it can be calculated as

$$\frac{1}{K_1^i} = \frac{L^i/2}{D_{eff}^i} + \frac{L^S/2}{D_{eff}^S} \frac{(\varepsilon_1^i + \varepsilon_p^i)}{(\varepsilon_1^S + \varepsilon_p^S)} \quad (4)$$

where, by convention, i will be anode or cathode, in that order; and m refers to particle size. It is important to emphasize that this coefficient arises from the previous manipulation of the written equations and is not a definition coming from a simplification. Conversely

$$D_{eff}^i = D_{e,o} \left(\varepsilon_1^i + \varepsilon_p^i\right)^{\gamma D,i} \quad (5)$$

is the effective coefficient of electrolyte phase diffusion.

It is noteworthy that summations in Eqs. 1 and 2 are extended for m particles.

The heretofore defined equations involve the volume fraction of phase j in compartment i: $\varepsilon_j^i$ is defined in the same way as reported in Ref. 7. In this work, however, a study where batteries are made up of different particle sizes is performed. Consequently, it is necessary to redefine the fractions of the different phases that constitute the electrodes. These definitions are explained below in the 'Multiparticle Model' section.

The contact area between spherical particles and electrolyte phase, and the volume of different phases are expressed by

$$a_{e/s,m}^i = 4\pi R_{s,m}^i{}^2 \tag{6}$$

$$a_{tr,e}^i = a_t\left(\varepsilon_l^i + \varepsilon_p^i\right) \tag{7}$$

$$v_e^i = a_t L^i\left(\varepsilon_l^i + \varepsilon_p^i\right) \tag{8}$$

$$v_s^i = a_t L^i \varepsilon_s^i \tag{9}$$

Following this line of work Ref. 7, where particles are discretized into three parts (internal, external, and surface), mass balance on electrode particles is

$$v_{ms,int}^i \frac{dC_{ms,int}^i}{dt} = \mp D_{ms}^i \frac{\left(C_{ms,int}^i - C_{ms,ext}^i\right)}{\left(\delta_{m,2}^i + \delta_{m,3}^i\right)} a_{m\,int}^i \tag{10}$$

$$v_{ms,ext}^i \frac{dC_{ms,ext}^i}{dt} = \pm D_{ms}^i \frac{\left(C_{ms,int}^i - C_{ms,ext}^i\right)}{\left(\delta_{m,2}^i + \delta_{m,3}^i\right)} a_{m\,int}^i \mp j_m^i a_{m\,ext}^i \tag{11}$$

$$C_{m\,surf}^i(t) = C_{ms,ext}^i(t) \mp j_m^i \frac{\delta_{m,4}^i}{D_{ms}^i} \tag{12}$$

where signs are consistent with the order of i. It is worth mentioning that $\delta_{m,j}^i$ are diffusion distances inside the particles, and their calculation may be consulted in Ref. 7 (Figure 4).

As can be seen, manipulation of the above equations has resulted in a mathematical model that should not be assumed to be a simplification of a p2d or similar models, but rather a new model arising entirely from an integral mass balance (in space) and differential in time of averaged properties. In this way, the set of equations that represent the evolution of concentrations (both in the compartments and in the particles), are equations that retain the character of differential in the field of time, but are integral equations in the space coordinates (both in the thickness of the electrodes as in the radius of the particles).

Simplified diagram concentration profiles of both electrolyte and particle phase can be seen in Ref. 7, Figures 3, and 4.

Conduction electrolyte properties are evaluated with the simplified expression A-2 of Ref. 3, used in Ref. 7 (Eq. 8)

$$\Delta\phi_e^A = -\frac{i_e^A L^A}{\kappa_{eff}^A} + \frac{RgT}{F}\left(1 - t_+^o\right)2\frac{\left(C_e^A - C_e^{A,S}\right)}{C_e^A} \tag{13}$$

being

$$\kappa_{eff}^i = \kappa_o^i\left(\varepsilon_l^i + \varepsilon_p^i\right)^{\gamma_{\kappa,i}} \tag{14}$$

the effective conductivity of electrolyte phase, and

$$\kappa_o^i = \left[\frac{\left(1 + K0\ C_e^i\right)^2}{\left(1 - K1\ C_e^i\right)^2 + \left(1 + K2\ C_e^i\right)^2 + K3}\right]\frac{1}{K4} \tag{15}$$

is conductivity of the salt solution. The parameters of Eq. 15 can be consulted in Table 2 of Ref. 7. This approach is preferred rather than the typical polynomial presented in Ref. 3 as it presents only one maximum conductivity value at normal working concentrations.

The potential drop in solid phase can be expressed as

$$\Delta\phi_{ms}^i = i_{ms}^i\ L^i / \sigma_{eff}^i \tag{16}$$

where effective conductivity $\sigma_{eff}^i$ is expressed as

$$\sigma_{eff}^i = \sigma_o^i\left(\varepsilon_s^i + \varepsilon_f^i\right)^{\gamma_{\sigma,i}} \tag{17}$$

Overpotentials are calculated by the Butler-Volmer equation

$$\eta_m^i = \frac{Rg\ T}{0.5\ F}\sinh^{-1}\left(\frac{j_m^i\ F}{2\ j0_m^i}\right),\ \text{with}$$

$$j0_m^i = k^i\left[C_{m\,surf}^i\ C_e^i\left(C_{m\,max}^i - C_{m\,surf}^i\right)\right]^{0.5} \tag{18}$$

and the total applied current, similarly to that shown in Ref. 7, is calculated by

$$i_{app} = F\ 4\ \pi\ \sum_m j_m^i n_m^i\ R_{s,m}^i{}^2 \tag{19}$$

As it will be seen later, it should be noted that, if the battery is composed of particles of a single radius, the fraction of the current drained by particles is equal to 1. However, if batteries have electrode particles of different sizes, fraction is a value between 0 and 1 for each different particle. Also, if the battery being studied is at a stage of charge, relaxation, or discharge, this fraction of current changes over time. Thus, it is defined as

$$\text{fraction}_m^i = j_m^i\ F\ 4\ \pi\ n_m^i\ R_{s,m}^i{}^2 / i_{app} \tag{20}$$

~~Conversely,~~ open circuit potentials vs. state of charge on both electrodes are represented by the functionality

$$\theta_m^i = C_{surf,m}^i / C_{max,m}^i \tag{21}$$

As in this study we will compare the results of our models against experimental data about batteries made of different electrode materials which were extracted from works by other authors, the equations used to represent the equilibrium potentials of different batteries are listed in the Appendix (Supporting Information).

AQ6

### Multiparticle model

In the first part of this work, the relationship between the numbers of particles is fixed

$$n_m^i / n_n^i \tag{22}$$

where i represents anode or cathode; and m and n identifies particle size.

In case of only two different particle sizes, namely "size 1" and "size 2," the following relations are used

$$\varepsilon_{s,m}^i = \frac{\varepsilon_s^i}{\left(R_{s,n}^i / R_{s,m}^i\right)^3 n_m^i / n_n^i + 1} \tag{23}$$

$$\varepsilon_{s,n}^i = \varepsilon_s^i\left(R_{s,n}^i / R_{s,m}^i\right)^3 n_n^i / n_m^i \tag{24}$$

and finally the number of each particle in electrodes is

$$n_n^i = \varepsilon_{s,n}^i\ a_t\ L^i / \left(4/3\ \pi\ R_{s,n}^i{}^3\right) \tag{25}$$

Electrolyte phase and solid phase currents are calculated as in Ref. 7, where

$$i_e^i = \frac{i_{app}/2}{\left(\varepsilon_l^i + \varepsilon_p^i\right)} \tag{26}$$

**Table 1. Adjustable Design Parameters Corresponding to Battery 1: $Li_xC_6|Li_yMn_2O_4$**

| Parameter | | Anode $Li_xC_6$ | Cathode $Li_yMn_2O_4$ | Separator |
|---|---|---|---|---|
| $\varepsilon_l$ | | 0.357 | 0.444 | 0.724 |
| $\varepsilon_p$ | | 0.146 | 0.186 | 0.276 |
| $\varepsilon_f$ | | 0.026 | 0.073 | |
| $L$ (cm) | | 0.01 | 0.0174 | 0.0052 |
| $\gamma_\kappa$ | | 3 | 3 | |
| $D_s$ (cm$^2$ s$^{-1}$) | | $3.9 \times 10^{-10}$ | $1.0 \times 10^{-9}$ | |
| $\sigma_0$ (S cm$^{-1}$) | | 1.0 | 0.038 | |
| $k$ (A cm$^{1/2}$ mol$^{-1/2}$) | | 0.18793 | 0.20803 | |
| $R_s$ (cm) | Particle 1 | 0.0013125 | 0.0008925 | |
| | Particle 2 | 0.001 | 0.00068 | |
| $\gamma_\sigma$ | | 1 | 1.5 | |
| $\gamma_D$ | | 3 | 3 | |
| $C_s^{max}$ (mol cm$^{-3}$) | | 0.02639 | 0.02286 | |
| $C_s^0$ (mol cm$^{-3}$) | | 0.01487 | 0.0039 | |
| $C_e^0$ (mol cm$^{-3}$) | | | 0.002 | |
| $D_e$ (cm$^2$ s$^{-1}$) | | | $1.51 \times 10^{-6}$ | |
| Ntpte | | | 0.363 | |

$$i_{s,n}^i = \frac{i_{app}/2}{\left(n_n^i \ \pi \ R_{s,n}^{i\ 2} + n_m^i \ \pi \ R_{s,m}^{i\ 2}\right)} \tag{27}$$

As it was discussed in Ref. 7, current density of electrolyte phase in the separator is expressed as

$$i_e^S = i_{app} \ a_t/a_{tr.e}^S \tag{28}$$

Taking into account the definition of overpotential and considering continuity of the electric field for particle "1" in contact with particle "2," then

$$U_{\theta,1}^i \pm \eta_1^i = U_{\theta,2}^i \pm \eta_2^i \tag{29}$$

where $(\pm)$ is function of the anode $(+)$ or cathode $(-)$.

Finally, the cell potential, considering that the battery consists of two-size particles, is calculated by

$$U_{cell} = \left(U_{\theta,1 \ or \ 2}^C - \eta_{1 \ or \ 2}^C\right) - \left(U_{\theta,1 \ or \ 2}^A + \eta_{1 \ or \ 2}^A\right) \\ - \Delta\phi_s^C - \Delta\phi_s^A - \Delta\phi_e^C - \Delta\phi_e^A - \Delta\phi_e^S \tag{30}$$

### Resolution of the Equations System

Batteries considered in this article have insertion electrodes whose particles can have different sizes. The general idea of resolution was developed considering that the batteries have only two particle sizes, but the same analysis can be easily extended to three or more different particle sizes. Likewise to Ref. 7, the calculation scheme was developed by setting constant current value and calculating cell potential over time. However, this scheme can be easily adapted for calculations in other conditions, for example, constant discharge power.

The calculus scheme was implemented in different programming environments to reduce errors. Gams,[30] was used to solve the system of equations simultaneously. A sequential and iterative calculation was implemented in SciLab.[31] Calculation times varied depending on the simulated current. For smaller currents (discharge times of about 40,000 s), normal computation times using the sequential scheme were 300 s. For higher currents, calculation times in discharge were 2 s on average. However, when the battery is in relaxation mode, calculation times were increased by 200 s. When the system was solved simultaneously with Gams, the calculation time was 2 s.

## Validation and Comparison with Experimental Data

For comparison with the experimental points, the developed model is used considering particles of two different sizes in each electrode. To achieve the results that best fit the experimental points, the following procedure was applied: one particle was left in its original size (reported in the corresponding paper), and the other particle size was varied. In some cases it was necessary to vary both particle sizes, with respect to its original size. In each of the cases treated, the corresponding details are reported.

This methodology can be extended to a distribution of particle sizes.

### Battery 1: $Li_xC_6|Li_yMn_2O_4$

In Ref. 7, the comparison with experimental data (Doyle et al.[3]) for two different cell types was presented, using a model that considers only a single particle size.

The experimental points were collected by the authors of Ref. 3 by performing constant current discharges. The two batteries used by the authors, differed mainly in the thickness of the electrodes, and the type of electrolyte used. Also in the original work, charging experiments were performed. However, they were not taken into account in our work.[7] In this article, we choose for our simulations, battery called as Cell 1 by the authors of.[3] Table 1 shows the physical parameters and the physicochemical properties representative for this battery. In addition, as we explain below, the particle sizes used in our simulations are detailed.

The particular focus of this section is to improve the quality of the comparison that we made in Ref. 7, considering this model, which takes into account two different particle sizes.

In all simulations performed with this model considering two particles sizes, the same amount of active material and the same fraction of solids in each electrode were fixed. Also the number of small particles was set equal to the number of large particles.

Comparisons with experimental results of battery discharge were slightly improved compared to the results presented in Ref. 7. To do that, a parametric sensitivity analysis was performed by varying the particle sizes in the simulations to achieve the best results. The chosen strategy was increasing
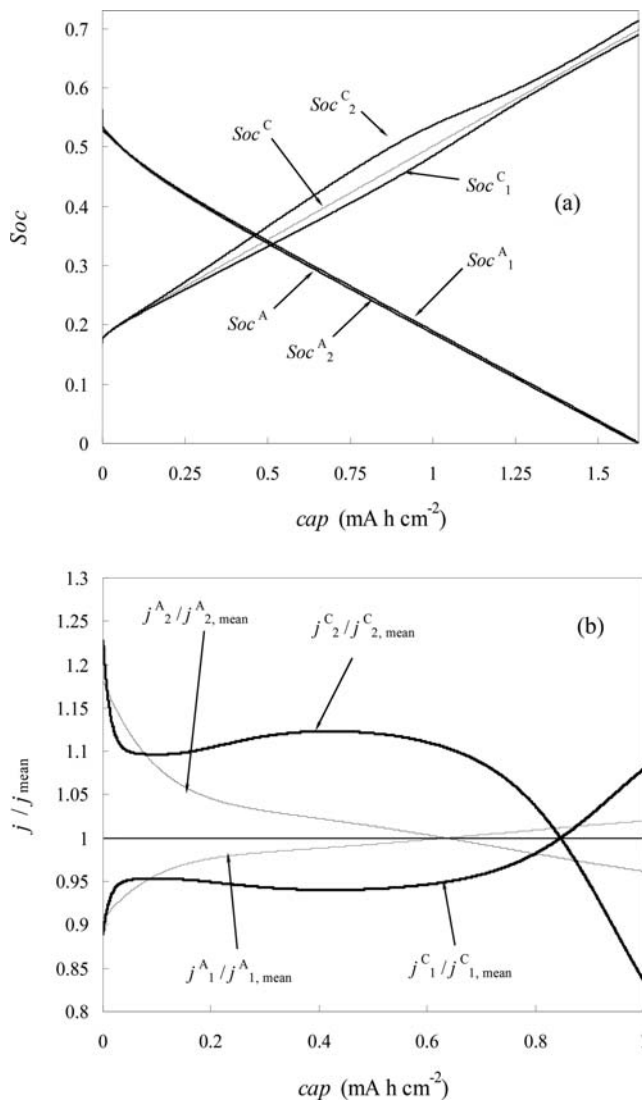
**Figure 1. Comparison of results considering one and two particle sizes. Battery 1: $Li_xC_6|Li_yMn_2O_4$. Particle 1: increased 5% and particle 2: decreased 20% from the original size (a) States of charge. $i_{app} = 0.0035$ $Acm^{-2}$ (b) Dimensionless electrochemical reaction rate. $i_{app} = 0.007$ $Acm^{-2}$.**

313 5% of the original size of the particle called "1," and reducing
314 by 20% the size of the particle called "2," from its original
315 size. These comparisons are not shown in this article as they
F6 316 are very similar to those shown in Ref. 7 (Figure 6a). How-
317 ever, the behavior of others physicochemical variables of these
318 batteries can be analyzed, considering these two different par-
F1 319 ticles sizes. Thus, in Figure 1a, the results of the evolution of
320 the states of charge ($Soc^i_{1\,or\,2}$) for a given discharge current of
321 anodic and cathodic particles compared to those produced con-
322 sidering a single particle size ($Soc^i$) are shown. Current densi-
323 ties and states of charge in cathodic particles are clearly
324 affected by the particle-size distribution. However, the average
325 value of the states of charge approaches the value of state of
326 charge of the battery considering a single particle size. Also,
327 in Figure 1b, the evolutions of dimensionless reaction rates are
328 displayed. These evolutions are affected significantly when
329 different particle sizes are considered. At the beginning of

330 discharge, reaction rates change significantly, ranging from
331 5% to 12% in a short time. Then the battery begins a period of
332 relatively little change in reaction rates, and the discharge is
333 controlled by ohmic losses. Finally, in the last stage of dis-
334 charge, a zone of great change in the variables is noticed.
335 These variations are most apparent for cathode particles and
336 are associated with shape potential equilibrium curve, as dis-
337 cussed below.

### Battery 2: $Li_xC_6|Li_yCoO_2$ 338

339 Experimental data of this kind of battery were extracted from
340 Ref. 8. The authors of this paper have used a Sony battery
341 18,650 With 1.8 Ah rated capacity. Experiments were conducted
342 similar to the case described above. The battery was charged to
343 an approximate voltage of 4.2 volts, and then it was discharged
344 at constant current conditions, to voltages near 2 volts.

345 In this article, the evolution of the performance of the bat-
346 tery with the number of cycles ($N$) at two different tempera-
347 tures was experimentally studied. In addition the authors
348 developed a mathematical model to fit the experimental points,
349 proposing semiempirical equations, which describe: the
350 change in state of charge, the change of film resistance, and
351 the change of the solid phase diffusion coefficient, as a func-
352 tion of number of cycles, for two different temperatures.

353 All parameters used to simulate this battery, were adopted
354 from Ref. 8, except:

   i. A model of the separator, which has the same potential 355
     drop as the one informed in the original work. 356
   ii. The initial state of charges. For anodic particles is 357
     0.838 and for cathodic particles is 0.375. 358

359 For comparison with experimental points of battery dis-
360 charge, the following strategy was selected: particles "2" are
361 larger than particles "1"; in the anode particle "2" is 80%
362 larger than the particle "1," and in the cathode particle "2" is
363 20% larger than the particle "1." Sizes of particle "1" was set
364 to the same value as in the original paper. These values, and
365 all the parameters used in the simulations for this battery, are
366 reported in Table 2. T2

367 The three empirical equations described in the original
368 paper (state of charge, particle diffusivity, and resistance) are
369 not used in our model. Instead, we simulated performance
370 loss, by decreasing the amount of particles as function on the
371 number of cycles.

372 Physically this loss of performance may be due to, electrical
373 contacts between some particles no longer exists, or due to the
374 formation of an extra resistance on the surfaces of the par-
375 ticles. This issue was widely discussed in the literature (e.g.[3]).

376 In our simulations, the number of particles "2" both in
377 anode and cathode diminishes as function of number of cycles.
378 Figures 2a, c shows the agreement between the experimental F2
379 points and the results of our model, at 25 and 50°C, respec-
380 tively. The larger particles in both anode and cathode,
381 decreases according to number of cycle, as it is shown in Fig-
382 ures 2b, 2d, for 25 and 50°C.

383 Therefore, in these simulations the total amount of active
384 material of the cell decreases as the number of cycles
385 increases. We assume that the active material lost, corresponds
386 to particles that lose electrical contact with neighbors
387 particles.

### Parametric Study using Two Particle Sizes 388

389 A parametric study is performance to identify the model
390 response under different discharge conditions. The simulated

**Table 2. Adjustable Design Parameters Corresponding to Battery 2: $Li_xC_6|Li_yCoO_2$.**

| Parameter | | Anode $Li_xC_6$ | Cathode $Li_yCoO_2$ | Separator |
|---|---|---|---|---|
| $\varepsilon_1$ | | 0.485 | 0.385 | 1 |
| $L$ (cm) | | 0.0088 | 0.008 | 0.008 |
| $D_s$ (cm$^2$ s$^{-1}$) | | $3.9 \times 10^{-10}$ | $1.0 \times 10^{-9}$ | |
| $\sigma_{eff}$ (S cm$^{-1}$) | | 0.005766 | 0.1211 | |
| $k$ (A cm$^{5/2}$ mol$^{-3/2}$) | | 0.2045 | 0.0981 | |
| $R_s$ (cm) | Particle 1 | 0.0020 | 0.0020 | |
| | Particle 2 | 0.0036 | 0.0024 | |
| $C_s^{max}$ (mol cm$^{-3}$) | | 0.030555 | 0.051555 | |
| $C_s^0$ (mol cm$^{-3}$) | | 0.02563[a] | 0.01933[b] | |
| $C_e^0$ (mol cm$^{-3}$) | | | 0.001 | |
| $D_e$ (cm$^2$ s$^{-1}$) | | | $7.5 \times 10^{-6}$ | |
| Area (m$^2$) | | | 0.0796 | |
| ntpte | | | 0.363 | |

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[a]Based on Data of Table 1[8]; $\theta^A_{initial} = 0.838$.
[b]Adopted from Table 1[8]; $\theta^C_{initial} = 0.375$.

391 battery, in this section, (considering only one particle size) is
392 detailed in Ref. 7, identified as cell A, and is the same battery
393 mentioned in the 4th section. In each section discussed below,
394 we detail the parameters changed, and the conditions these
395 changes were made.
396    In this article we consider that each electrode contains par-
397 ticles of two different sizes: Particles of size "1" called par-
398 ticles "1" and particles of size "2" called particles "2."
399    The methodology used in this study consists of setting particle
400 size "1" for both anodic and cathodic electrodes, in its original

401 size (shown in Table 1, according with the experiments and sim-
402 ulation of the original paper), and varying particle size "2." The
403 total amount of solid material is maintained constant in both
404 anode and cathode. This condition is imposed from the above
405 Eqs. 22–29, in which the total solid fraction remains constant in
406 each electrode. Furthermore, the number of particles "1" is set
407 equal to the number of particles "2." As a consequence, the total
408 number of particles diminishes as the size of particles "2"
409 increases. According to these constraints, all following compari-
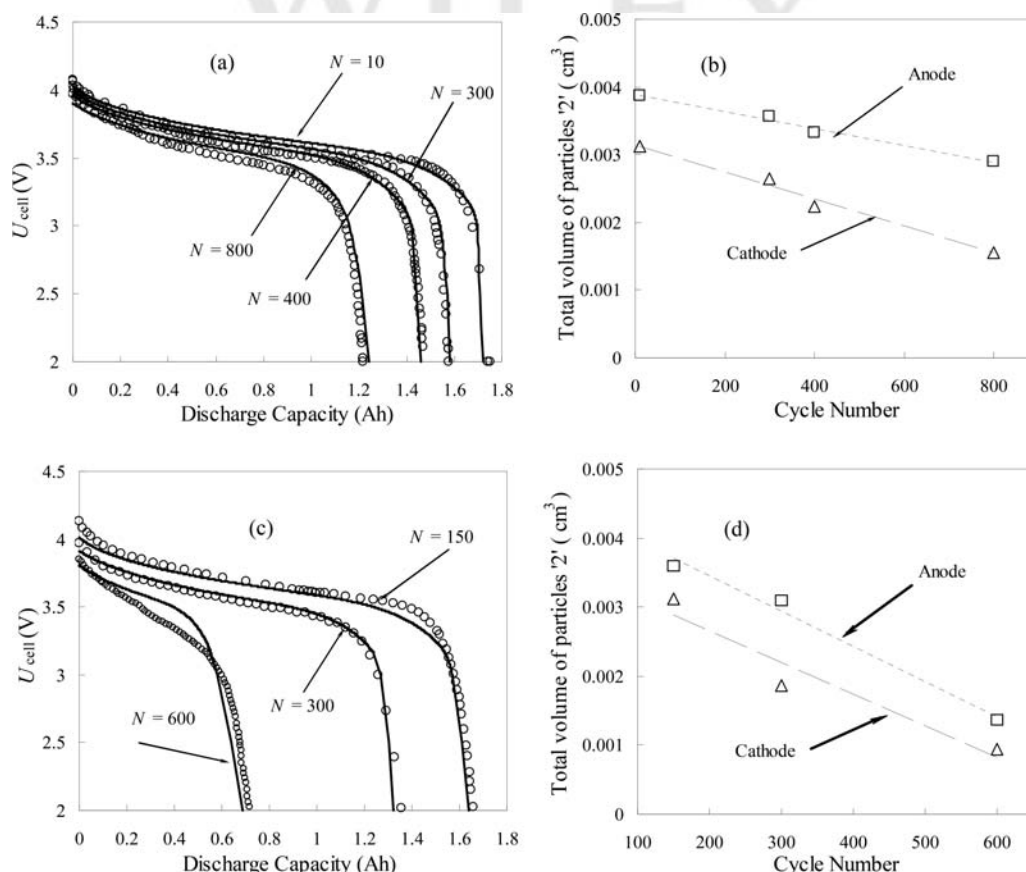410 sons involve batteries with the same amount of active material.



**Figure 2. Comparison between experimental points[8] and the model developed in this article Battery 2: $Li_xC_6|Li_{y}$-$CoO_2$.**

(a) and (b) $T = 25°C$. (c) and (d) $T = 50°C$ Left: Cell potential. Right: Deactivation of solid phase (particle '2').
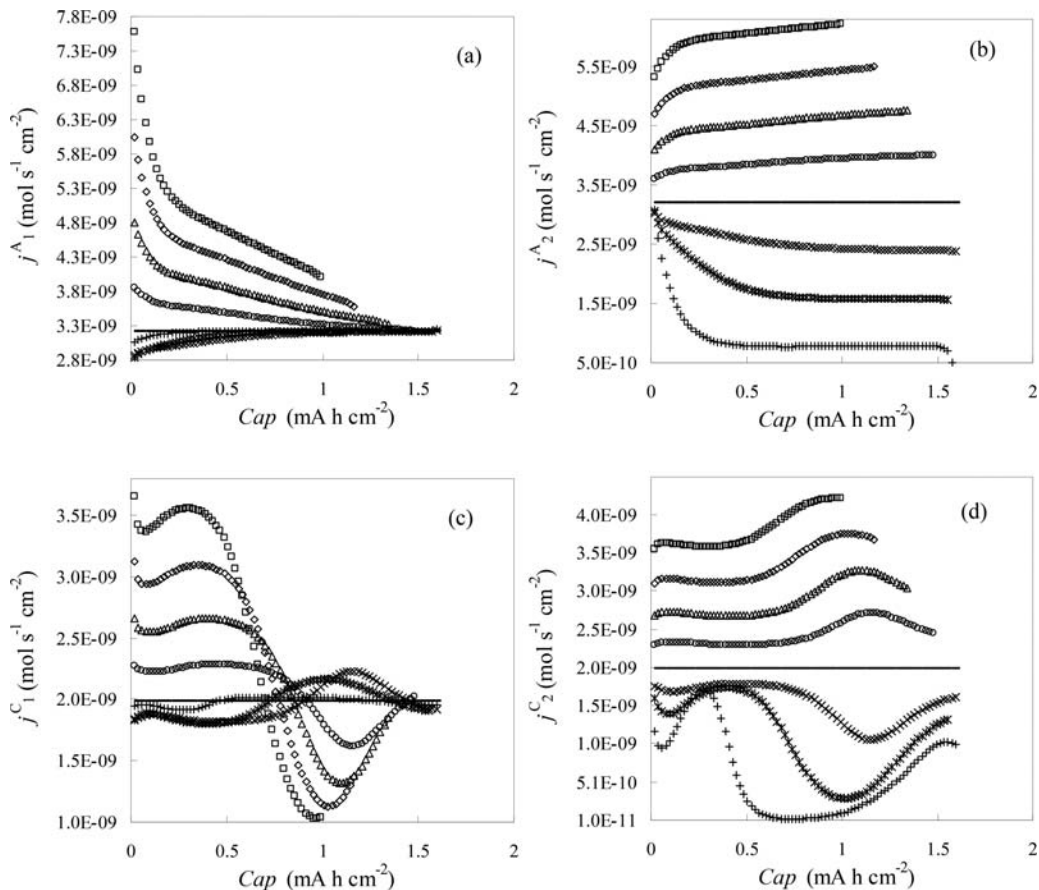
**Figure 3. Evolution of reaction rates at constant discharge current, considering two particle sizes. $i_{app}$ = 0.0035 Acm$^{-2}$.**

(a) Particle 1 in anode. (b) Particle 2 in anode. (c) Particle 1 in cathode. (d) Particle 2 in cathode. Square: $R_{s,2}/R_{s,1}$ = 2.00. Rhombus: $R_{s,2}/R_{s,1}$ = 1.75. Triangle: $R_{s,2}/R_{s,1}$ = 1.50. Circle: $R_{s,2}/R_{s,1}$ = 1.25. Line: $R_{s,2}/R_{s,1}$ = 1.00. Cross: $R_{s,2}/R_{s,1}$ = 0.75. Star: $R_{s,2}/R_{s,1}$ = 0.50. Plus sign: $R_{s,2}/R_{s,1}$ = 0.25.

### Cell voltage

Cell voltage was calculated at a representative constant discharge current of 0.000875 Acm$^{-2}$, until it reaches a value below 1.5 V, and considering different particle-size ratios ($R_{s,2}/R_{s,1}$ = 3.00; 2.00; 1.75; 1.50; 1.25; 1.00; 0.75; 0.5). As the ratio of sizes is greater, the battery performance is negatively affected. For example, battery which has particle-size relation equal to 2, reduces its final capacity in nearly 10% against a battery with uniform particle sizes, which implies an approximate reduction time of 12 min, for this cell configuration (discharging times of a battery, considering a single particle size can be corroborated in Ref. 7 Table 4). And another whose particle-size relation is equal to 3, worsens its performance by almost 27% compared to that has no size distribution, which it involves 34 min less on operation. If the battery is discharged to intermediate discharge rate (0.0035 Acm$^{-2}$) the final capacity would decrease by about 50% comparing $R_{s,2}/R_{s,1}$ = 2.00 vs. $R_{s,2}/R_{s,1}$ = 1.00 cases. And if the battery is discharged to the higher simulated current (0.007 Acm$^{-2}$), the reduction of performance, would be around 60%, analyzing the same aforementioned case.

### Reaction rate

Figure 3 shows the evolution of anodic and cathodic electrochemical reaction rates which are parametric to the relations between particle sizes. Figures 3a, b corresponds to anodic particles 1 and 2, respectively. Figures 3c, d corresponds to the cathodic particles. The lines that appear with no variation correspond to simulations that consider both particles of the same size. The scheme of particle-size variation is similar to that previously described. Particle size 1 remained constant and particle size 2 was varied.

Figure 3a shows that the higher the quotient size—greater than 1—, the higher the initial rate on particle 1 and the reaction rate over time on particle 1. Consequently, there is a greater amount of converted lithium inside particles at the initial instants; and the battery is discharged faster. When the relationship between sizes is lower than one, initial velocities become smaller and the battery capacity is increased. In the latter cases, however, it is initially observed that the trend is not as expected as there is an apparent crossing of initial reaction rates and reaction rates over time. In Figure 3b, the same trends can be seen. On the contrary to what happens with particle 1, velocities increase over time for ratios greater than 1 and decrease for ratios lower than 1. Here, it can be observed the importance of having a simplified model with phenomenological significance to analyze the behavior of these variables. In the same compartment, while some particles increase their electrochemical lithium conversion rate, others decrease. It can be seen on the left-hand scale of Figures 3a, b that the reaction rates of both particles are cross linked when the battery is about 25% of its discharge, considering the largest dispersion between the sizes.

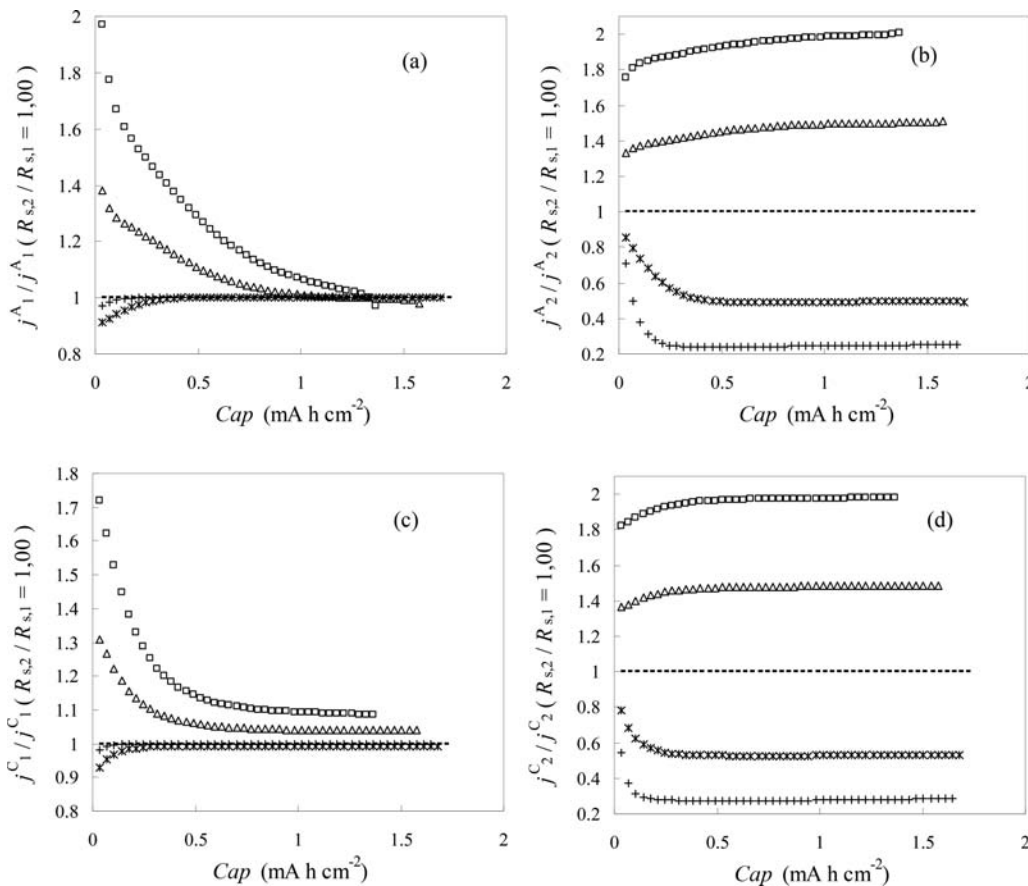**Figure 4. Evolution of reaction rates at constant discharge current, considering Eq. 35. $i_{app} = 0.00175$ Acm$^{-2}$.**

(a) Particle 1 in anode. (b) Particle 2 in anode. (c) Particle 1 in cathode. (d) Particle 2 in cathode. Square: $R_{s,2}/R_{s,1} = 2.00$. Triangle: $R_{s,2}/R_{s,1} = 1.50$. Line: $R_{s,2}/R_{s,1} = 1.00$. Star: $R_{s,2}/R_{s,1} = 0.50$. Plus sign: $R_{s,2}/R_{s,1} = 0.25$.

Reaction rates of cathodic particles are more complex to be analyzed, as, as shown in Figures 3c, d, there is a temporal evolution crossing. These crossings are due to the Plateau shape of the cathodic equilibrium potential (Eq. A2). To avoid this masking caused by the oscillations of these Plateaus, Eq. A2 is replaced by an equation arising from a logarithmic fit of these points without inflexion points

$$U_\theta^C = -0.153 \; LN(\theta^C) + 3.955 \qquad (31)$$

The dimensionless reaction rate for a typical value of intermediate current for some values of radius ratio is shown in Figure 4. Dimensionless reaction rate refers to a cell working with particles of the same size. With this modification in the $U_\theta$ equation, cathodic behavior becomes similar to anodic one. Reaction rates for particle 1 both in cathode and anode show unexpected crossing for radius ratios lower than 1. This situation is related to the difference in external surface area of electrodes. In fact, comparisons performed up to this point involve batteries with the same active material volume and the same number of particles. Analysis of batteries with the same active material volume and the same electrode surface area is presented forward.

### *Capacity*

Comparisons performed in the last section correspond to batteries with different particle sizes and the same amount of active electrode volume. A further condition was imposed by defining the number of particles "1" equal to the number of particles "2." To assess the impact of particle-size difference, batteries with the same electrode surface area will be compared instead of batteries with equal number of particles. Under this new frame, particle-size distribution becomes a variable. The problem can be defined as: Given the batteries showing the same dimensions and the same volume of active material and the same external surface area of electrodes, capacity will be computed for different particle sizes and, consequently, for different number of particles. Figures 5a, b show battery capacities discharging at constant current for different number of particles "1" and "2" which are parametric with the number of the other particle. In this study, radius "1" are lower than radius "2" but the number of particles "1" are not necessarily greater than number of particles "2." Figure 5a shows two different regions depending on the value of $n_1^A$. For values greater than $6e^5$, the greater the number of particles "2," the higher the capacity, while for values lower than $6e^5$, the greater the number of particles "2," the lower the final capacity. Conversely, Figure 5b depicts a different behavior, the higher the number of particles "1" for a given number of particles "2," the lower the capacity. These tendencies can be easily explained resorting to the computation of a parameter defined as: difference in particle radius divided by the average particle radius. Figure 5c shows this parameter as function of number of particles computed in the simulations of Figures 5a, b. This parameter is a measure of the impact of particle-size distribution for batteries with the same amount of active material and the same electrode surface area. The greater the radius difference, the worse the battery performance.
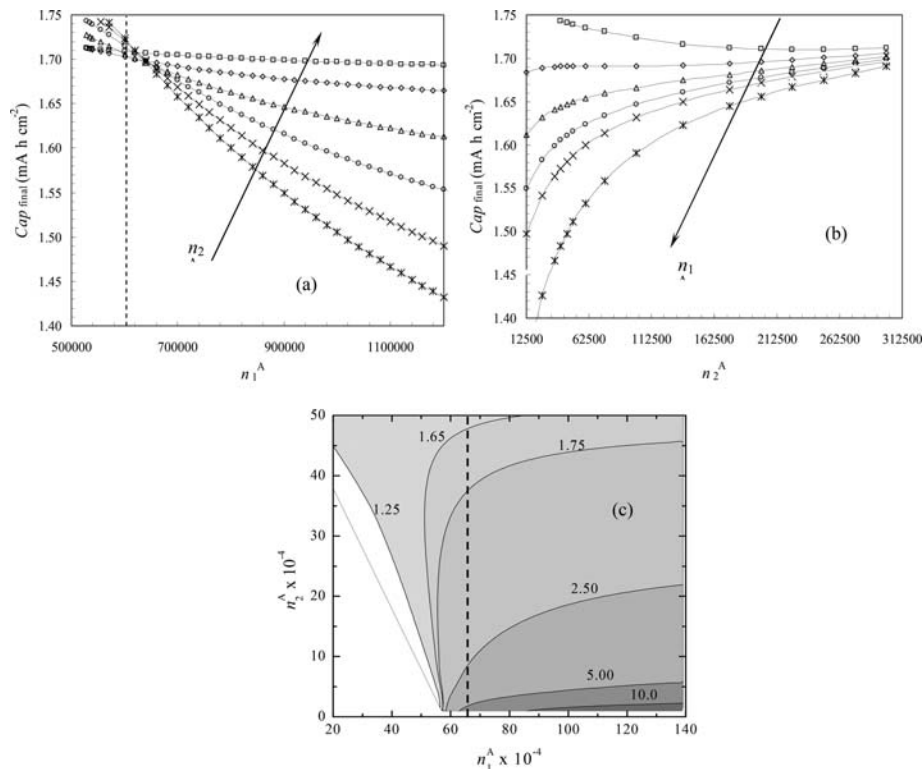
**Figure 5. Battery final capacities as a function of.**

(a) the number of particle "1" with the number of particle "2" as a parameter. Square: $n_2^A = 3,00,000$. Rhombus: $n_2^A = 2,00,000$. Triangle: $n_2^A = 1,00,000$. Circle: $n_2^A = 50,000$. Cross: $n_2^A = 25,000$. Star: $n_2^A = 12500$. (b) the number of particle "2" with the number of particle "1" as a parameter. Square: $n_1^A = 54,00,00$. Rhombus: $n_1^A = 66,00,00$. Triangle: $n_1^A = 7,80,000$. Circle: $n_1^A = 90,0000$. Cross: $n_1^A = 1,020,000$. Star: $n_1^A = 1,50,0000$. (c) Level curves of abs $(R_{s,1}^A - R_{s,2}^A)* (R_{s,1}^A + R_{s,2}^A)$. $i_{app} = 0.00175$ Acm$^{-2}$.
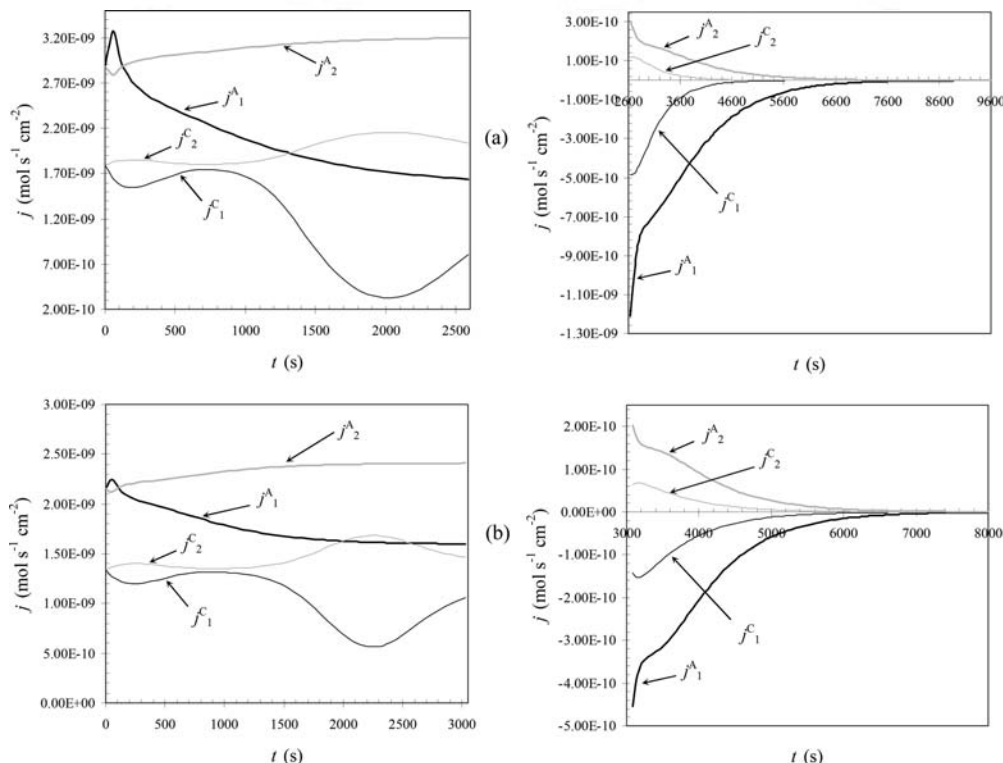


**Figure 6. Reaction rate evolution at a constant discharge current and for two-size relations. Left: discharge. Right: without current.** $i_{app}$: 0.00175 mA cm$^{-2}$.

(a): $R_{s,2}/R_{s,1} = 2.00$. (b): $R_{s,2}/R_{s,1} = 1.50$.

## Results of the Model Considering Relaxation

As it was discussed in Ref. 7, relaxation times in the process of discharge of a battery are very important due to the physico-chemical phenomena that influence the next batteries cycles (charges or discharges). If the electrodes of a battery have particles of different sizes, it is expected that these phenomena are more radically affected.

To study the characteristic variables of the battery, constant current discharges up to 2.7 volts were simulated. Batteries involve particles "1" and "2" with the same amount of active material and the same number of particles "1" and "2." Once discharge was turned off, variables involved in the simulations were computed as a time function.

The simulation results in cell voltage, indicate that the higher the relationship between particle radius, the lower the battery final capacity. Furthermore, voltage restitution after relaxation time is smaller when the ratio of particle size is smaller.

For example, for a typical low current discharge (0.000175 $Acm^{-2}$), a battery with uniform particle size, would be discharged at 637 min, while a battery with $R_{s,2}/R_{s,1}=2$ is discharged in 622 min. Likewise relaxation times in battery with uniform particle size, would be relatively short, approximately 7 min. And 48 min for the case $R_{s,2}/R_{s,1} = 2$. If the same calculation is performed for a discharge current slightly higher, 0.00175 $Acm^{-2}$, the discharge times are 3400 and 2600 s and the relaxation times are 450 and 2200 s, respectively ($R_{s,2}/R_{s,1} = 1$ and $R_{s,2}/R_{s,1} = 2$).

Once again, the importance of having a model such as the one presented in this paper is evident, to predict these phenomena. This model, differential in time, integral in space, allows us to evaluate this dramatic change in the total duration of the charge of the battery, being subjected to a controlled discharge at constant current. It can be inferred that if the discharge is performed under nonideal conditions (e.g., with the discharge and recharge cycles typical of an electric car) these discrepancies would be even greater.

This fact would indicate, once more, that battery performance is negatively affected by particle-size distribution in the electrodes. That is, even though the batteries with higher ratios between particle sizes reach a relative higher voltage at the relaxation stage, their delivered capacity was lower and they took longer to reach the new equilibrium state.

Figure 6 depicts the evolution of reaction rates for an intermediate current and for two values of particle-size relationships before and after the discharge of the battery. Discharge periods were analyzed in previous sections. At relaxation moments, an abrupt reduction of current densities takes place (note differences in the graph scales). Anode particles take longer to reach the equilibrium; and this phenomenon is more evident for the battery of Figure 6a, wherein the dispersion among particle sizes of electrodes is the greatest, again indicating the negative contribution of this size difference.

Finally, Figure 7 shows, the values taken by the overpotential of the different particles of both electrodes, Figure 7a, and ~~conversely,~~ the difference in equilibrium potentials of both electrodes, Figure 7b. This analysis is performed for a typical current value and a typical size distribution value.

Figure 7 also depicts the behavior of the continuity of the electric field Eq. 29 both in discharge zone and relaxation zone. The abrupt jump in the values of variables is detected around 3000 s after discharge. Again, it becomes evident that relaxation of anode particles (thicker lines, Figure 7a) takes



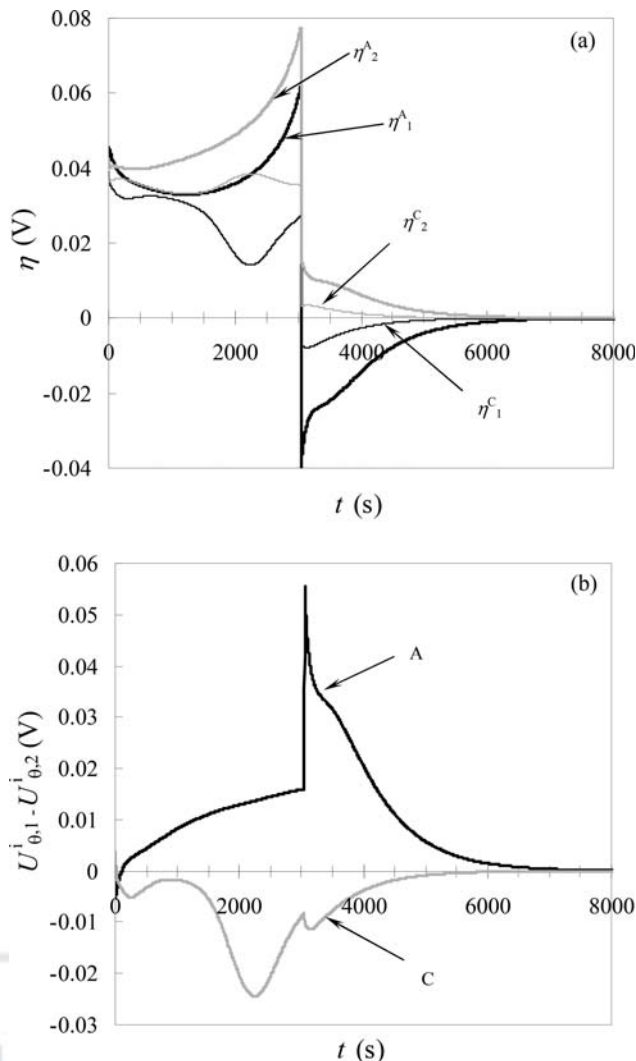**Figure 7. Continuity of electric field.**

(a) overpotentials. (b) difference in equilibrium potentials $i_{app}$: 0.00175 mA cm$^{-2}$. $R_{s,2}/R_{s,1} = 1.50$.            AQ8

longer than that of cathode particles. This effect can be explained by taking into account the different shapes of equilibrium potentials, $U_\theta$, and the fact that anode particles are larger than cathode particles in these batteries. So, finally, there is evidence to account not only for the size of particles themselves, but also for the distribution of particle sizes in electrodes.

The negative influence of particle-size distribution on the electrodes of a lithium-ion battery has been demonstrated, which is the attained objective of this study.

Furthermore, evidence has been provided for the importance of addressing these factors in battery manufacturing.

## Conclusions

1. The performance of lithium ion was studied by solving a novel mathematical model in two different scenarios: (i) maintaining constant the amount of active electrode material and varying the particle size, (ii) maintaining constant volume and the electrode surface area and varying the number of each of the particles.

2. This model has been validated by experimental points provided by other authors and using two different types of cells.

3. With this simplified model, large discrepancies in the final duration of a battery considering different particle sizes and batteries with a homogeneous particles sizes were found. This feature is much appreciated for predicting the behavior of batteries in large facilities.

4. Some comparisons between the model and the experimental points were significantly improved by varying the particle sizes of the electrodes.

5. Plateaus existence in the cathode equilibrium potential impacts markedly in the current density distribution between particles of different sizes.

6. Differences between particles sizes of the electrodes, negatively affects the performance of the battery. At high discharge current, difference between the particle sizes of 50%, reduces up to 35% battery capacity.

7. By maintaining constant the number of one particle type, significant variations in battery capacity are obtained by varying the number of the other particle, keeping constant the total amount of material.

8. Relaxation times of a partially discharged battery are also affected by the fact of having particles with different sizes. Relaxation occurs 25% faster on batteries with uniform particle size, comparing them against batteries that have a dispersion size of 100%.

## Acknowledgments

## Notation

$a$ = area, cm$^2$
Cap = capacity, mA h cm$^{-2}$
$C$ = concentration, mol cm$^{-3}$
$i$ = current density, mA cm$^{-2}$
$D$ = diffusion coefficient, cm$^2$ s$^{-1}$
$F$ = Faraday's constant: 96485.34, C mol$^{-1}$
$j$ = electrochemical reaction rate, mol s$^{-1}$ cm$^{-2}$
$j_0$ = exchange current density, mA cm$^{-2}$
$K$ = constants in Eq. 15
$K_l^i$ = mass transfer coefficient between anode (i = A) and separator and separator and cathode (i = C), cm s$^{-1}$
$k$ = constant rate of the electrochemical reaction
$k_i$ = (i = 1; 2; 3; 4) = constants in Eqs. 31–33
$L$ = electrode length, cm
$n$ = number of solid particles
ntpte = transport number
$N$ = usage cycle
$U$ = potential, V
$R$g = universal gas constant 8.314, J mol$^{-1}$ K$^{-1}$
$R_f^0$ = resistance between particles, Eq. 34
$R_{s,m}^i$ = solid particle radius of the particle "m" on the electrode "i", cm
$t$ = time, s
$T$ = temperature, K
$v$ = volume, cm$^3$

### Specials and Greek letters

$t_+^o$ = transport number
$f_\pm$ = molar activity coefficient of the salt
$\varepsilon$ = volume fraction
$\delta$ = diffusion distance, cm

$\kappa$ = electrolyte conductivity, S cm$^{-1}$
$\Delta\phi$ = potential drop, V
$\sigma$ = solid conductivity, S cm$^{-1}$
$\theta$ = state of charge
$\eta$ = overpotential, V
fraction = fraction of the current drained by particles

### Subscript

app = applied
e = electrolyte
eff = effective
e/s = electrolyte in contact with solid
n, m = particle number
s = solid
f = filler
p = polymer
l = liquid
tr.e = transversal area of electrolyte phase
tr.s = transversal area of solid phase
t = transversal
o = pure
$\theta$ = open circuit potential
cell = cell
diff = diffusion
int = interior
ext = exterior
max = maximum
surf = surface

### Superscript

i = anode, cathode or separator
A = anode
C = cathode
S = separator
$\gamma$ = Bruggeman's exponent
0 = initial
o = pure

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