A mass-preserving Sliding Mode Observer for Li-ion cells electrochemical model

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Abstract— An advanced Battery Management System (BMS) is required to operate lithium-ion (Li-ion) batteries efficiently and safely. Such a BMS should estimate the cells internal states (residual charge, temperature, ions concentrations) accurately and, at the same time, with a reduced computational cost. In this work, the concentrations in a Li-ion cell are estimated via a Sliding Mode Observer (SMO) applied to the electrochemical Single Particle Model (SPM); thanks to the selected model solution technique, this setup offers accurate estimations of both distributed and bulk quantities, with high computation efficiency. The observability issue of SPM is overcome by a new two-step algorithm for the design of the observer gain matrix. This algorithm aims at preserving the total lithium mass estimated by the SMO. The proposed approach is validated in simulation with currents as high as 10C.

I. Introduction

Lithium-ion (Li-ion) batteries represent nowadays the most adopted technology for both (hybrid) electric vehicles and consumer electronics. In fact, they offer outstanding energy and power densities compared to other chemistries. However, the materials employed to manufacture Li-ion cells suffer from chemical instability and are subject to possible over-heating and even explosion. To deal with their nature, Li-ion cells require an advanced Battery Management System (BMS) for accurate measurements, estimations and monitoring of the battery pack. Currently, the BMS design approach is often conservative, because available estimations of the cell states are not accurate enough. Thus, the BMS is not capable of exploiting the full potential of the battery. To improve the cell performances without renouncing safety, accurate modeling, parameters identification and state estimation algorithms are needed.

The main components of a Li-ion cell are: negative electrode, positive electrode and separator [1]. The electrodes have a lattice structure and are immersed in the electrolyte (usually liquid). The separator is a porous electron-insulating film. The functioning process of Li-ion cells is called *dual-intercalation* [2], and is described shortly in what follows. During cell discharge, lithium diffuses to the surface of negative electrode active material particles, where the electron-generating reaction takes place. Electrons are conducted by the solid lattice to the current collectors, and then through the load to the positive electrode. Li-ions dissolve in the electrolyte, flow towards the separator and cross it. Eventually,

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Li-ions and electrons are reabsorbed by positive electrode active material particles.

In the literature, several Li-ion cells models can be found, characterized by their complexity and accuracy (for example, see [3]): from the simple *grey-box* Equivalent Circuit Models (ECMs) ([4], [5]), to complex *first-principle* Computational Fluid Dynamics (CFD) models (extremely accurate, but at a high computational cost). As opposed to current practice, standard battery operations could be significantly improved if limitations were applied to reactions overpotentials instead of on terminal voltage only (as also shown in [3]), which requires a sufficiently accurate model, with insight on the electrochemical reactions that take place inside the cell. In [6], it was highlighted that, in particular, the crucial information, needed to effectively avoid locally critical depletion levels, is internal lithium concentration gradients. The Pseudo 2-Dimensional (P2D) model, originally formulated in [7], is an electrochemical model, widely recognized as a valuable trade-off between detailed modeling and computational burden. However, relying on Partial Differential Algebraic Equations (PDAEs), the P2D model poses some limitations in the implementation and in the observer formulation [8]. According to available literature [9], the whole model or the solid phase diffusion dynamics can be approximated and/or reduced with several methods (*e.g.* assumption of parabolic concentrations profiles in solid phase [10], impedance model of solid phase and Finite Elements Method applied to electrolyte phase [11]). Probably, the most popular approach is the Single Particle Model (SPM) [12], that neglects the electrolyte dynamics and assumes that each electrode is composed by a single spherical particle. It offers an electrochemical description of the reactions taking place inside the cell, but adopting more simple Partial Differential Equations (PDEs) instead of PDAEs. In this work, a SPM is adopted and solved according to the technique presented in [13], which encompasses a spectral method for the model spatial discretization and the PDEs approximated solution. This approach is extremely efficient in terms of the cell dynamics simulation, and it maintains the physical meaning of all the variables and parameters.

State estimation techniques come in diverse complexity and accuracy flavors, depending on that of the employed model. Some works employ linearized/reduced/simplified P2D models, combined with Kalman observers (*e.g.*, impedance-based model with linear Kalman Filter in [6], reduced-order model with Extended Kalman Filter in [14], volume-averaged model with Unscented Kalman Filter in [15]). All these approaches are characterized by a high

model and observer structural complexity, which increases the effort for designing and properly tuning the state estimation algorithm. Also, computational time may be a crucial issue in such complex systems. Instead, the use of SPM in combination with advanced state estimation concepts, as proposed in the well investigated work [8], greatly reduces the computational cost related to the observation problem. This cost can be further decreased by employing, in combination with SPM, efficient state estimation algorithms, among which Sliding Mode Observers (SMOs) are of sure appeal [16], [17]. In fact, they are endowed with a minimal complexity and with immediate results interpretation. SMOs have been extensively applied to ECMs of Li-ion cells, which lead to reduced estimation capabilities (for example, in [18] only bulk SoC is estimated). To the best of the authors' knowledge, the only successful application of SMO to an electrochemical Li-ion cell model is due to [19]. There, based on the SPM, SoC is estimated together with a few physio-chemical parameters. However, the proposed algorithm has limited validity, in that it is built on two strong model simplifications: 1) to increase model observability, only one electrode is considered; 2) the dynamics of concentrations at the core of the active material particle is neglected. In the present work, a SMO is applied to the complete SPM, *i.e.* no model simplifications are introduced. Also, a novel two-step algorithm for the design of the observer gain matrix is introduced, which overcomes the SPM observability issue by enforcing total lithium mass conservation in SMO estimation. The resulting state observer provides, in addition to the estimate of SoC, the estimate of lithium concentration profiles along particles radii in both electrodes, at a minimal computational cost.

This paper is organized as follows. In Section II, the SPM is presented, and the solution method by [13] is briefly recalled. In Section III, the structure of the SMO applied to the SPM is first presented; then, two alternative methods to design the observer gain matrix are proposed: a uniform correction and a mass-preserving algorithm. In Section IV, the novel approach is fully validated in simulation. Finally, conclusions are drawn in Section V.

II. SINGLE PARTICLE MODEL

In the SPM, the dual-intercalation process is described by a set of PDEs, only considering the diffusion dynamics that take place inside the spherical particles, along the *radial direction r*. These dynamics are ruled by *Fick's law*:

$$\frac{\partial c_{s,i}}{\partial t} = \frac{D_{s,i}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{s,i}}{\partial r} \right) \tag{1}$$

where c_s is the concentration of lithium in solid phase; D_s is the solid phase diffusion coefficient; subscript $i = \{n,p\}$ is used, here and in the following, to indicate negative or positive electrode, respectively. The boundary conditions at the particle core and surface are, respectively:

$$\left. \frac{\partial c_{s,i}}{\partial r} \right|_{r=0} = 0 \qquad \left. D_{s,i} \frac{\partial c_{s,i}}{\partial r} \right|_{r=R_{s,i}} = \frac{-j_i^{Li}}{a_{s,i}F}$$

where a_s is the specific interfacial area and F is Faraday's constant. j^{Li} is the molar flux at particle surface, and is related to the input current I as follows:

$$j_n^{Li} = \frac{I}{a_{s,n}FA\delta_n} \qquad j_p^{Li} = -\frac{I}{a_{s,p}FA\delta_p} \tag{2}$$

where A is the electrode plate area and δ is the electrode thickness. The overpotential η can be computed from the inversion of *Butler-Volmer kinetics equation*, under the commonly accepted hypothesis of equal charge transfer coefficients in the two electrodes ($\alpha_n = \alpha_p = 0.5$):

$$\eta_i = \frac{2RT}{F} \sinh^{-1} \left(\frac{F}{2j_{0,i}} j_i^{Li} \right)$$

where R is the universal gas constant; T is the lumped cell temperature; j_0 is the exchange current density. Finally, the output voltage is given by:

$$V = (U_p + \eta_p) - (U_n + \eta_n) - \frac{R_f}{A} I \tag{3}$$

where R_f is the film resistance of the electrode plate and U is the thermodynamic equilibrium potential, a non-linear function of surface concentration c_{ss}. In the following, the subscript *ss* denotes the superficial element of concentration, *i.e.* $c_{ss,i} = c_{s,i}(r = R_{s,i})$, while the subscript *sc* denotes the core element of concentration, *i.e.* $c_{sc,i} = c_{s,i}(r = 0)$.

It is also useful to introduce the definition of stoichiometry, that is the normalized version of concentration over the maximum value $c_{s,i}^{max}$:

$$\theta_{s,i} = \frac{c_{s,i}}{c_{s,i}^{max}}$$

and the definition of bulk State of Charge (conventionally computed on negative electrode):

$$\text{SoC} = \frac{\left(\frac{3}{R_{s,n}^3} \int_0^{R_{s,n}} r^2 \theta_{s,n} \, dr \right) - \theta_{s,n}^{0\%}}{\theta_{s,n}^{100\%} - \theta_{s,n}^{0\%}}$$

where $\theta_{s,n}^{0,100\%}$ are the values of stoichiometry, respectively, at 0 and 100% SoC.

The SPM is discretized in space and solved via *Chebyshev orthogonal collocation* spectral method. Here we summarize only the main steps behind this approach, while the reader may refer to [13] for a complete discussion on the method and its computational details. Essentially, the proposed method consists in the following steps:

1) A proper change of variables is introduced and the diffusion equations are written accordingly.
2) A system of linear ODEs is obtained and solved thanks to Chebyshev differentiation matrices, which allow to approximate PDEs solutions as polynomials at the $N_c + 1$ Chebyshev nodes (here $N_c = 20$ is set).
3) The non-linear output equation of the model is analogous to (3) (that is, a function of the linear system outputs and of the input current).

As part of the first step introduced above, a new state vector is defined in place of $c_{s,i}$, with a suitable change of variables:

$$\omega_i = r c_{s,i} \tag{4}$$

so that the diffusion equation (1) can be rewritten, after defining $\rho = r/R_{s,i}$, as:

$$\frac{\partial \omega_i}{\partial t} = \frac{D_{s,i}}{R_{s,i}^2} \frac{\partial^2 \omega_i}{\partial \rho^2}.$$

Secondly, gradients of ω_i along ρ are approximated thanks to Chebychev differentiation matrices C_1 and C_2, for first and second derivative, respectively:

$$\frac{\partial \omega_i}{\partial \rho} \approx C_1 \omega_i$$

$$\frac{\partial^2 \omega_i}{\partial \rho^2} \approx C_2 \omega_i.$$

In this way, the system is formulated in state-space form as:

$$\begin{cases} \dot{\omega}_i = A_{\omega,i} \omega_i + B_{\omega,i} j_i^{Li} \\ c_{s,i} = C_{\omega,i} \omega_{s,i} + D_{\omega,i} j_i^{Li} \end{cases} \tag{5}$$

where $A_{\omega,i}, B_{\omega,i}, C_{\omega,i}, D_{\omega,i}$ are the state-space matrices obtained from manipulation of C_1 and C_2. $c_{s,i}$ is considered as the output of the reformulated linear system. Eventually, a single state vector Ω is defined as the concatenation of ω_n and ω_p. Also, since $c_{s,i}$ is a linear function of the state ω_i and of the input I, equation (3) can be properly rewritten to obtain the final state-space representation of the cell model:

$$\begin{cases} \dot{\Omega} = A_\Omega \Omega + B_\Omega I \\ V = h(\Omega, I) \end{cases} \tag{6}$$

where A_Ω is obtained by concatenating matrices $A_{\omega,i}$ and B_Ω by concatenating matrices $B_{\omega,i}$ and scaling them according to equations (2). The obtained model has a linear state transition equation and a non-linear output function.

III. SLIDING MODE OBSERVER DESIGN

The objective of this section is to estimate concentrations inside the spherical particles, which are unmeasurable quantities, based on the SPM and measured output voltage. A generic SMO approaches this problem by implementing a copy of the model (6) and injecting a discontinuous correction term on the state transition equation. Indicating with $\hat{\Omega}$ and $\hat{V}$, respectively, the estimated state and output of the system, the following observer structure is obtained:

$$\begin{cases} \dot{\hat{\Omega}} = A_\Omega \hat{\Omega} + B_\Omega I + M_\Omega v \\ \hat{V} = h(\hat{\Omega}, I) \end{cases}$$

where v is the discontinuous injection term, while M_Ω is the observer gain matrix, to be designed so as to drive to zero in finite time the *sliding variable* defined as:

$$\sigma = e_V = V - \hat{V}$$

which is the output voltage estimation error. The injection term is simply given by:

$$v = \text{sign}(e_V).$$

Note that, since it is difficult to give a physical interpretation to correction terms on states ω_i, the actual implementation of the SMO proposed here acts directly on $c_{s,i}$. This is done as follows: 1) the system (5) is implemented in discrete time and, at each time step, concentrations $c_{s,i}$ corresponding to simulated states ω_i are computed as per the output equation; 2) corrections are applied to $c_{s,i}$, according to SMO strategy; 3) the initial states ω_i for the next time step are computed from the corrected $c_{s,i}$ through the definition (4). Details are skipped for the sake of brevity. In the following exemplifications, correction terms are thus designed directly on $c_{s,i}$, which can be better understood by the reader. Thus, a new observer gain matrix M_C is introduced, so that $M_\Omega = r M_C$.

The proposed SMO is based on the following assumption:

Assumption: It is reasonable to assume that a positive estimation error on V is due to a positive estimation error on $c_{s,n}$ and to a negative estimation error on $c_{s,p}$. In fact, V is, respectively, a monotonically decreasing and monotonically increasing function of U_n and U_p, appearing in output function $h(\cdot)$. In turn, U_n and U_p are monotonically decreasing functions, respectively, of $\theta_{ss,n}$ and $\theta_{ss,p}$ (see [20] for some examples of such functions for different cell chemistries). In symbols, this assumption can be expressed as:

$$e_V > 0 \Rightarrow \begin{cases} \hat{c}_{s,n} < c_{s,n} \\ \hat{c}_{s,p} > c_{s,p} \end{cases}$$

where $\hat{c}_{s,i}$ is the estimated concetration. This assumption extends the one made by [19] to the case with two electrodes.

A. SMO with uniform correction

One simple choice for matrix M_C is a scalar gain m multiplying a vector of "+1"s in all $N_c + 1$ positions corresponding to $c_{s,n}$ and "-1"s in all $N_c + 1$ positions corresponding to $c_{s,p}$:

$$M_C = m \begin{bmatrix} +1 & \dots & +1 & -1 & \dots & -1 \end{bmatrix}^T. \tag{7}$$

This implies that the correction of concentrations takes place uniformly along r for all elements of both negative and positive electrodes, with proper sign, as depicted in Figure 1. However, the SPM is characterized by a poor
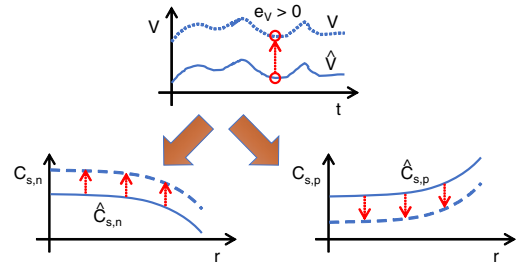

Fig. 1. Concentrations correction in SMO, with M_C designed as in (7).

observability of the core concentration of active material particles from the measured voltage, as analyzed by [8]. Also, the uniform injection mechanism in SMO does not guarantee the conservation of total lithium mass in the cell. In fact, concentration is corrected in the two electrodes with

a certain gain, with proper sign, but without any information on how much lithium is withdrawn from an electrode and how much is supplied to the other one, due to the injection term (recall that, in general, the physio-chemical and geometrical characteristics of the two electrodes are different). Thus, without any additional enforcement of lithium mass conservation, the total mass of lithium in SMO soon moves from its initial value, and state estimate does not converge to an acceptable result. A simulation study is reported here to confirm this issue.

The test consists in a pulse discharge at 0-10C (i.e. 10 times the nominal current of the cell, defined as I/Q, where Q is the cell rated capacity), starting from a fully charged cell (SoC$_0$ = 100%), with pulses and rests of 10s duration. The SMO is initialized with a 20% error in SoC (SoC$_{0,SMO}$ = 80%). The following state estimation errors are introduced, for surface and core stoichiometries, respectively, for both electrodes:

$$e_{ss,i} = \theta_{ss,i} - \hat{\theta}_{ss,i}$$
$$e_{sc,i} = \theta_{sc,i} - \hat{\theta}_{sc,i}$$

Although the sliding variable e_V is driven to zero in about 9s, as shown in Figure 2 (top), the state estimates do not converge to the "true" values, as exemplified in Figure 2 (center-bottom) for surface stoichiometries. This behavior is
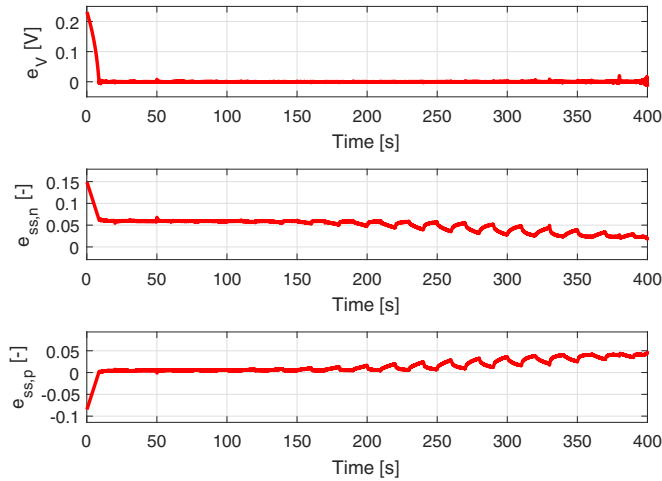

Fig. 2. Estimation errors for SMO with uniform correction (top: output voltage; center: negative electrode surface stoichiometry; bottom: positive electrode surface stoichiometry).

explained by investigating the number of moles of lithium stored in each electrode; for the SPM, this can be computed as:

$$n_{s,i} = \frac{3A\delta_i\varepsilon_{s,i}}{R_{s,i}^3} \int_0^{R_{s,i}} r^2 c_{s,i} \, dr$$

where ε_s is the solid-phase volume fraction, while the total number of moles of lithium stored in the cell is the sum of those of the two electrodes:

$$n_s = n_{s,n} + n_{s,p}.$$

In order for n_s to remain constant, any variation in $n_{s,n}$ should be compensated by an equal and opposite variation in $n_{s,p}$,

and *vice-versa*. Figure 3 shows $n_{s,n}$, $n_{s,p}$ and n_s during the previous test, for both simulated cell and SMO. In discharge conditions, as those considered here, negative electrode is emptying with lithium, while positive electrode is getting filled; however, here, there is a clear decrease in n_s in the first part of the simulation for SMO with uniform correction. This means that the variations in $n_{s,n}$ and $n_{s,p}$ are not balanced with such observer design.
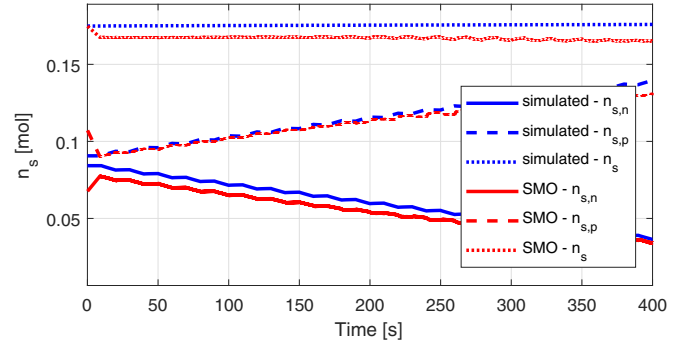

Fig. 3. Mass conservation problem in SMO with uniform correction: number of moles of lithium available in negative electrode, positive electrode and cell.

B. SMO with mass-preserving correction

The algorithm proposed here has the objective of overcoming the above limitations of SMO applied to the SPM. It enforces total lithium mass conservation, by designing M_C according to the following two steps:

1) correct all $N_c + 1$ elements of $c_{s,n}$ as in (7);
2) correct each element k (for $k = 1..N_c + 1$) of $c_{s,p}$ enforcing null mass variation w.r.t. the k-th element of $c_{s,n}$.

Importantly, the correction on $c_{s,p}$ has the same sign as in (7), but with a pondered gain design. While step 1 above is trivial, step 2 needs an analysis on electrode properties. Although the SPM describes the dynamics of only one sphere in each electrode, the lattice structure is composed of hundreds of millions particles. Based on the cell parameters, the number of active material spheres in each electrode can be computed as the ratio of effective electrode volume over the volume of an individual sphere:

$$N_i^{sph} = \frac{A\delta_i\varepsilon_{s,i}}{\frac{4}{3}\pi R_{s,i}^3}.$$

When the correction term is applied to the k-th element of $c_{s,n}$, a variation in lithium concentration is obtained (w.r.t. just the open-loop state transition), which is called $\Delta c_{n,k}$. This means that all spheres in negative electrode are receiving such a variation in concentration at position k along r (recall: SPM does not distinguish among spheres along cell thickness direction). The overall variation of the number of moles of lithium available in the negative electrode at position k is thus given by:

$$\Delta n_{n,k} = \Delta c_{n,k} N_n^{sph} V_{n,k}^{sec} \qquad (8)$$

where $V_{n,k}^{sec}$ is the volume of the k-th spherical sector in negative electrode. To ensure mass conservation, the correction term of the k-th element of $c_{s,p}$ should lead to a variation in lithium moles equal and opposite to that of the k-th element of $c_{s,n}$:

$$\Delta n_{p,k} = -\Delta n_{n,k}.$$

Finally, with a similar reasoning as that applied to write (8), the corresponding variation in lithium concentration in positive electrode is found as:

$$\Delta c_{p,k} = \frac{\Delta n_{p,k}}{N_p^{sph} V_{p,k}^{sec}} = -\frac{\Delta c_{n,k} N_n^{sph} V_{n,k}^{sec}}{N_p^{sph} V_{p,k}^{sec}} \quad (9)$$

which is the correction term to be applied to the k-th element of $c_{s,p}$ to exactly balance the k-th injection term of $c_{s,n}$. In this way, the total mass of lithium available in the cell is conserved. Notice that, as opposed to the strategy presented in Section III-A, the correction of concentrations is not uniform in positive electrode, and it is an explicit function of that applied to the negative electrode, as depicted in Figure 4. Equation (9) represents a general strategy to correct $c_{s,p}$ enforcing total mass conservation, even when $c_{s,n}$ is corrected with a different strategy from the one presented here (step 1 above). The following section validates this algorithm with
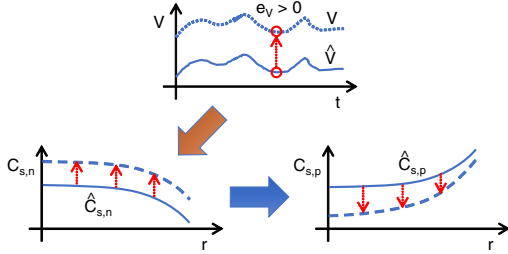

Fig. 4. Concentrations correction in SMO, with M_C designed as described in Section III-B.

a simulation study.

IV. VALIDATION

This section validates the mass-preserving SMO presented in the previous section. The considered test is the same as described in the previous section (pulse discharge at 0-10C starting from a fully charged cell). Figure 5 shows the sliding variable and the injection variable in mass-preserving SMO, for different values of the scalar gain m (applied only on negative electrode, as explained earlier). The following considerations can be drawn:

- *sliding mode* of variable e_V is successfully enforced;
- *reaching time* (defined in the Sliding Mode literature as the time needed by σ to reach zero for the first time) is linearly decreasing with observer gain: it is roughly 1.5s, 15s and 150s, respectively, for $m = 10^{-2}$, 10^{-3} and 10^{-4};
- on the other hand, the higher is m, the more evident are oscillations around zero of e_V, especially towards the end of simulation (where output equation is more

non-linear); in other words, lower values of m entail a longer *reaching time*, but a more stable estimation;
- during sliding, variable v exhibits high-frequency switching, which is typically named *chattering phenomenon* in Sliding Mode literature; this phenomenon is usually not critical for estimation problems.
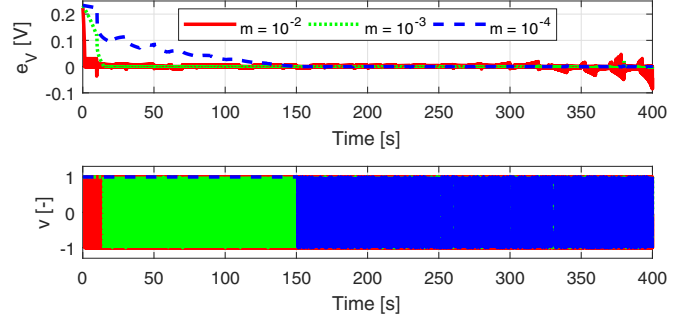

Fig. 5. Output voltage estimation error (top) and injection variable (bottom) for SMO with mass-preserving correction, for different values of gain m.

Thanks to the designed SMO algorithm, not only e_V is driven to zero, but also all state estimation errors defined earlier (and all other elements along r, not shown here for space reasons). The result of state estimation convergence are presented in Figure 6 for surface stoichiometries and in Figure 7 for core stoichiometries. Notice that the same properties described for e_V hold true in these cases as well. Given the convergence of
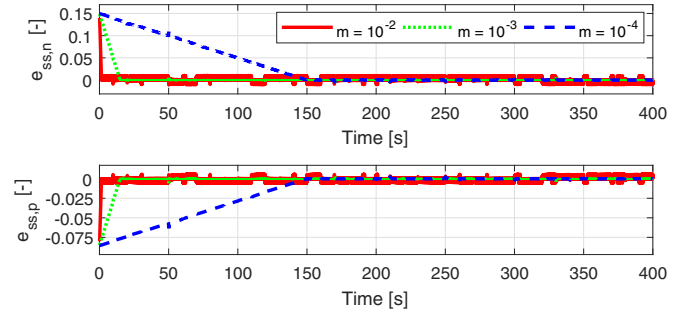

Fig. 6. Surface state estimation errors for SMO with mass-preserving correction (top: negative electrode; bottom: positive electrode), for different values of gain m.
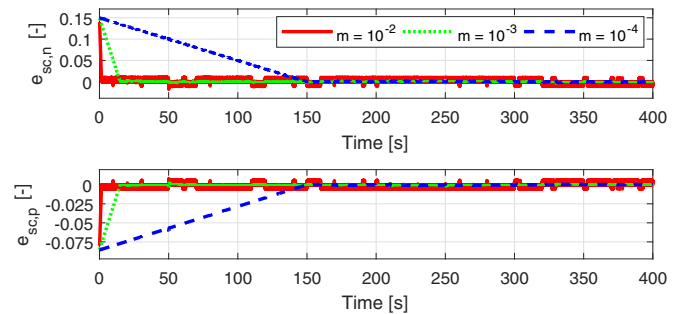

Fig. 7. Core state estimation errors for SMO with mass-preserving correction (top: negative electrode; bottom: positive electrode), for different values of gain m.

state estimations, it follows immediately that SoC estimation is also converging, with the same properties as observed above, as shown in Figure 8.
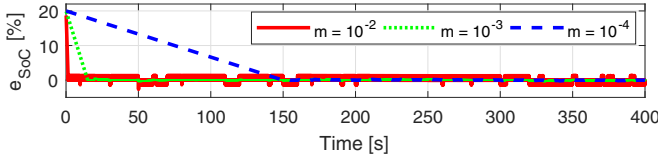

Fig. 8. State of Charge estimation errors for SMO with mass-preserving correction, for different values of gain m.

To test the mass-preserving SMO estimation robustness, the above test is repeated with additive measurement noise acting on V. The noise is white, with null mean and variance equal to 1mV. Even in this scenario, state estimation errors converge to zero, as shown in Figure 9 (only surface stoichiometries are reported, for space reasons). However, the following considerations are due:

- reaching time is longer than without measurement noise;
- oscillations are present on state estimates, as expected, along the entire duration of the test, which are filtered by lower values of gain m;

As such, a trade-off is clearly observed, which was less prominent without noise: a lower gain m leads to slower convergence of state estimates, but also to less noisy signals (filtering effect of state observer is enhanced).
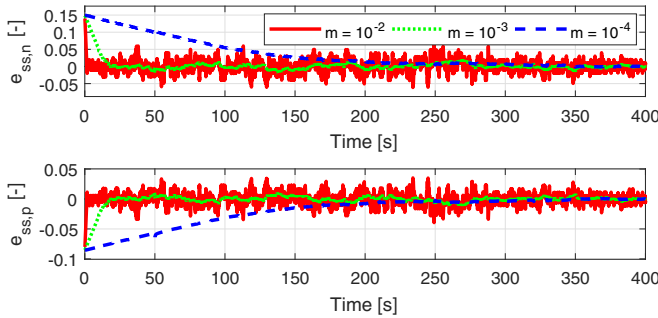

Fig. 9. Surface state estimation errors for SMO with mass-preserving correction and noisy measurements (top: negative electrode; bottom: positive electrode), for different values of gain m.

V. CONCLUSIONS

In the present work, a SMO is applied to the electrochemical SPM. A mass-preserving design algorithm is proposed for the choice of the SMO gain matrix. This enables to overcome the observability issues associated with SPM, and to successfully estimate lithium concentrations profiles along particles radii and bulk State of Charge. The obtained results are confirmed with noisy output voltage measurements.

As a future work, the algorithm robustness w.r.t. model parametric uncertainty may be investigated as well. Also, further oscillations suppression in estimated states may be achieved by designing a second-order SMO. A natural application of the proposed algorithm is the implementation on a real-world BMS, thanks to its inherent computational efficiency.

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