Governing equations for a two-scale analysis of Li-ion battery cells

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A B S T R A C T

This contribution describes a computational homogenization approach to model the multi-physics processes in Li-ion batteries in a multi-scale view. The adopted approach originates from the fundamental balance laws (of mass, momentum, charge) at both scales and the multi scale analysis roots itself on an energy-based weak formulation of the balance laws, which allows to extend the Hill–Mandel energy averaging theorem to the problem at hand. Electroneutrality *assumption* has been taken into account. Maxwell's equations are considered in a *quasi-static sense* in a rigorous setting. *Time dependent scale transitions* are formulated, as required by the length/time scales involved in Li-ion batteries processes, while *scale separation in time* is argued. Constitutive assumptions, computational procedures and simulations will be collected in a companion paper.

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1. Introduction

Developing the next generation of batteries for higher capacity and longer life of cycling is one of the strategic challenges facing the energy storage planning of mankind. Li-ion batteries currently have the highest energy storage density of any rechargeable battery technology (Scrosati and Garche, 2010). They are based on the classical intercalation reaction during which Li is inserted into or extracted from electrodes. Large volume changes are associated with this process. They induce inelastic effects (Sethuraman et al., 2010; Sethuraman et al., 2012), phase-segregation (Wang et al., 2013; Matthew, 2013), micro-cracks and particle fracture (Kalnaus et al., 2011), decrepitation or pulverization, loss of integrity and loss of electric contact with the current collector. This compromises the widespread application for the next generation batteries and limits their use to relatively low power applications such as portable devices.

An electrochemical cell necessarily consists of several phases (Newman and Thomas-Alyea, 2004) – a sketch of a Li-ion battery cell is shown in Fig. 1. They must include two electrodes, a separator, and an electrolytic solution. An *electrode* is a material in which electrons are the mobile species. An electrolyte is a material in

which the mobile species are ions and in which the free movement of electrons is blocked. The latter flow in the external conductor and finally travel through the electrodes, doing work or requiring energy. A binary ionic compound is a salt consisting of only two elements in which both elements are ions, a cation (which has a positive charge) and an anion (which has a negative charge). An electrolyte that contains only one solvent and one salt is called a *binary electrolyte*. Mass must be transported through the electrolyte from one electrode to the other to bring reactants to the interfaces. Mass transfer in an electrolytic solution requires a description of the movement of mobile ionic species. In the absence of *convection*, as assumed henceforth, movement of species is governed by *diffusion*, driven by gradients of concentration, and by *migration* driven by an electric field for any charged particles.

Stress evolution, diffusion, and fracture have been investigated in recent publications. In Cheng and Verbrugge (2009) and Cheng and Verbrugge (2010) the diffusion equation is solved independently and the stress distribution is estimated according to small strain linear elastic theory. Elastic stresses and fracture resulting from the interactions between particles undergoing swelling have been included in more recent models (Aifantis and Dempsey, 2005; Purkayastha and McMeeking, 2012). Li metal alloys, e.g. silicon (Li–Si), and tin (Li–Sn), are appealing classes of materials for the next generation of Li-ion batteries, due to their specific capacity which largely exceeds that of conventional anodes based on graphite. Experimental observations show that the alloys active particles experience phase transitions and large deformations while lithiated

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(Huang et al., 2010; Sethuraman et al., 2010; Liu et al., 2012; Nadimpalli et al., 2014). As a consequence, plastic deformations arise, making an elastic characterization of the material unrealistic for those classes of materials. A vast amount of literature deals with experiments and modeling of single particles for these classes of materials - to cite but a few (Christensen and Newman, 2006; Zhang et al., 2007; Zhao et al., 2011; Chon et al., 2011; Liu et al., 2011; Liu et al., 2012; Zhao et al., 2012; Anand, 2012; Cui et al., 2013; Suo et al., 2013; Huang et al., 2013; Drozdov, 2014; Drozdov, 2014; Mukhopadhyay and Sheldon, 2014; Di Leo et al., 2014; Marcicki et al., 2014). Recent works Bower and Guduru (2012) and Bucci et al. (2014) also account for crack propagation in active particles subjected to lithiation and for SEI layer formation across the electrode/electrolyte interface.

To avoid the complexity of the non-uniform intercalation within each active particle, it is customary in literature to restrict the analysis to *one-dimensional* problems, eventually focusing to nano-wires (Ryu et al., 2011), thin films (Bucci et al., 2014), or to a single active particle without modeling the surrounding material and phenomena; neither the electrolyte nor the interface reaction are directly considered, but the electrochemical interactions are replaced by "a priori" given incoming flux, often assuming axi-symmetry.

Analysis of stress affecting Li-ion batteries have been carried out also at larger scales. Examples can be found in Zhang et al. (2012), where diffusion-induced stress in a layered structure (multilayer electrode plate including active plates as well as current collector) has been investigated and in Sahraei et al. (2012), Wierzbicki and Sahraei (2013) and Sahraei et al. (2014) where the structural response of battery cells subjected to externally applied mechanical stresses has been analyzed.

The approach pursued in this paper is different from the literature cited above, since it focuses on the multi-scale and multi-physics modeling of the whole battery cell whereby no a priori restrictions are required for the geometry of battery components. A few other papers share the same target (Doyle et al., 1993; Garcia et al., 2005; Wang and Sastry, 2007; Golmon et al., 2009; Christensen, 2010; Renganathan et al., 2010; Bower et al., 2011; Golmon et al., 2012; Ferguson and Bazant, 2012). The behavior of the battery cell is intrinsically multi-scale, as the multi-physics phenomena involving diffusion, migration, intercalation, and the accompanying mechanical effects take place at the characteristic length scale of the electrode compound, which is three orders of magnitudes smaller than the battery cell size. Directly resolving all scales and modeling all particles in the electrodes is computationally unfeasible. Instead, the nano-scale effects are incorporated into the micro-scale problem through constitutive models that are derived from advanced homogenization methods. Golmon et al. (2009, 2012) considered the Mori–Tanaka approach at a meso-scale; Hashin–Strickman as well as Wiener bounds have been considered by Ferguson and Bazant (2012).

In a recent contribution, Salvadori et al. (2014) a computational homogenization technique (Suquet et al., 1985) was tailored to Li-ion batteries by using a multiscale scheme with a complex multi-particle representative volume element (RVE). Such an approach allows to model explicitly the electrochemical interactions that take place at the interface between particles in which neutral Lithium is stored and the electrolyte in which ionic Lithium moves together with its salt counter-ions driven by diffusion and migration. Those chemical reactions, that take place in a very narrow layer termed after Stern, Goüy and Chapman, are ultimately responsible for the state of charge of batteries. The latter turns
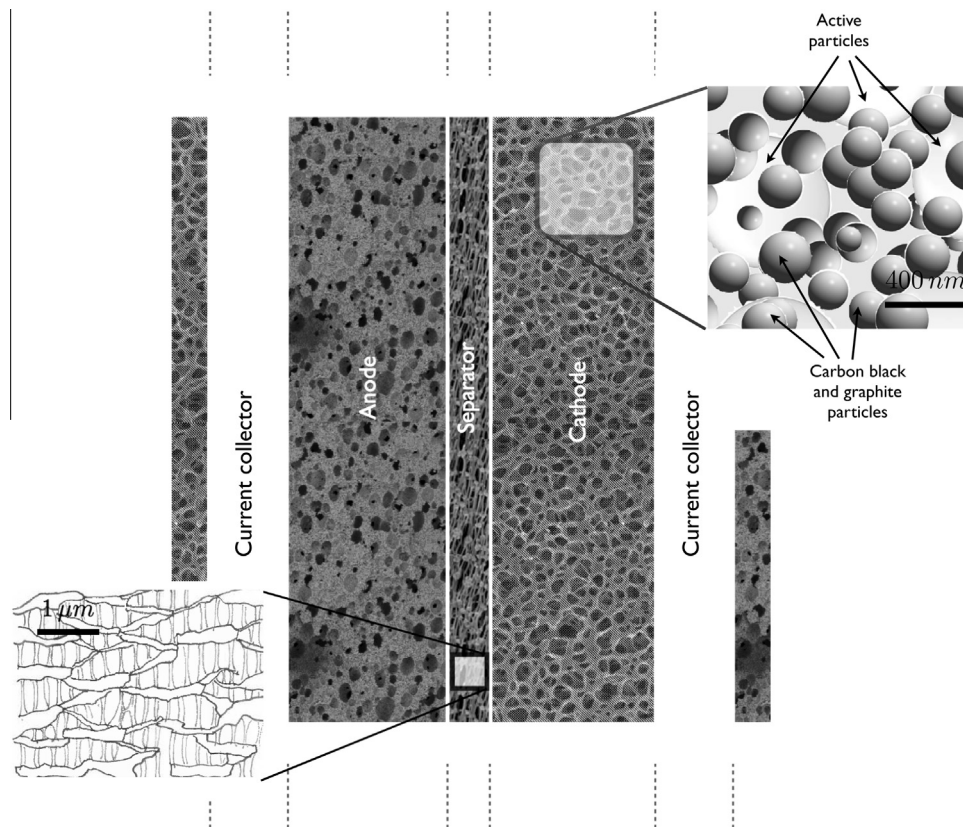

Fig. 1. Sketch of a Li-ion battery cell with porous electrodes. Additives are used to create conductive networks in both electrodes, to increase the electronic conductivity. Additives include large (graphite) and small (carbon black) conductive particles, that are bound to the active particles that host Lithium by a polymer binder (PVDF for instance). Separator scanning electrode microscope images can be found for instance in Wu et al. (2014).