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On Nonlinear Modelling of Structural Battery Composites

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Abstract

Structural battery composites are multifunctional materials with the ability to simultaneously store electrochemical energy and carry mechanical load. A conventional lithium-ion battery comprises a positive electrode, a separator, and a negative electrode. The constituents are soaked in a liquid electrolyte, allowing lithium-ion exchange between the electrodes while electrons travel through an external circuit via current collectors. In structural batteries, the negative electrode is replaced by multifunctional carbon fibres, enabling the additional function as mechanical reinforcement. The liquid electrolyte is replaced by a porous two-phase matrix material. The solid polymer phase transfers mechanical loads between the carbon fibres, and the lithium ions travel in the liquid phase, occupying the pores in the polymer matrix. Redox reactions occur on the electrode/electrolyte interfaces. For instance, reduction of lithium ions forms neutral lithium that diffuses inside the carbon fibres in a charge process of a structural battery full cell. Lithium insertion is accompanied by extensive carbon fibre expansion, which causes internal stresses and affects the elastic moduli of the carbon fibres. In contrast, applying a mechanical load to the lithiated carbon induces a response in the electric potential.

In the first paper, we study the effect of the carbon fibre expansion on the surrounding matrix material in a structural negative electrode. In particular, we investigate the significance of adopting non-linear kinematics. In this way, features such as the internal stress state, homogenized tangent stiffness, and expansion of the homogenized negative electrode can be predicted.

The second paper concerns multiphysics modelling of a structural battery full cell, that is, a $LiFePO_4$ (lithium-iron-phosphate) based positive electrode against a carbon fibre negative electrode. Specifically, we introduce non-linear reaction kinetics to describe the redox reactions occurring on the electrode / electrolyte interfaces. Moreover, we discuss coupled electro-chemo-mechanical modelling of the positive electrode and the pertinent calibration towards experimental findings.

Keywords: Li-ion battery modelling; Multifunctional materials; Computational homogenization; Coupled problems; Model calibration.

List of Publications

This thesis is based on the following publications:

[A] **Carl Larsson**, Fredrik Larsson, Johanna Xu, Kenneth Runesson, Leif E. Asp, "Effects of lithium insertion induced swelling of a structural battery negative electrode". *Composites Science and Technology*, Vol no. 244, no. 11, 2023, 0266-3538.

[B] **Carl Larsson**, Fredrik Larsson, Johanna Xu, Kenneth Runesson, Leif E. Asp, "An Electro-Chemo-Mechanical Model for Analysis of Structural Battery Composite Full Cells". Manuscript.

Other publications by the author, not included in this thesis, are:

Mohammad Siam Siraj, Samia Tasneem, David Carlstedt, Shanghong Duan, Marcus Johansen, **Carl Larsson**, Johanna Xu, Fang Liu, Fredrik Edgren, Leif E Asp. "Advancing structural battery composites: robust manufacturing for enhanced and consistent multifunctional performance". *Advanced Energy and Sustainability Research*, 2300109, 2023.

Preface

The work in this thesis was carried out from February 2022 to May 2024 in the Division of Material and Computational Mechanics, Department of Industrial and Materials Science, Chalmers University of Technology. The research was financially supported by the US Air Force through the EOARD Award No. FA8655-21-1-7038.

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Furthermore, I would like to thank my colleagues in the division of Material and Computational Mechanics, M2 Dynamics, and M2 Fluid Dynamics for making the day-to-day experience at work so enjoyable.
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Contents

Part I

Extended Summary

CHAPTER 1

Introduction

1.1 Background

Structural battery composites offer a novel approach to energy storage and structural integrity within a single material system. Unlike traditional batteries, which are typically separate components within a system, e.g. an electric vehicle, structural battery composites have potential to integrate into the very structure of the system they power [1]–[4]. This integration eliminates the need for bulky external battery packs, resulting in lighter and more streamlined designs with enhanced efficiency. In this way, structural batteries provide the ability to effectively store and deliver electrical energy and, at the same time, provide structural support.

The key components of structural battery composites include multifunctional carbon fibres with Li-storing capabilities, which conduct electricity and mechanically reinforce the composite material [5]–[8]. These fibres replace traditional negative electrode materials, such as graphite, found in conventional batteries. Additionally, the porous matrix material consists of a solid phase for mechanical load transfer and a liquid phase that facilitates ion transport between electrodes during charge and discharge [9]–[12]. Furthermore, the

positive electrode consists of active lithium iron phosphate ($LiFePO_4$, LFP) material and conductive particles adhered to an aluminium foil. These components together constitute the structural battery composite illustrated in Figure 1.1, showing a charge process.

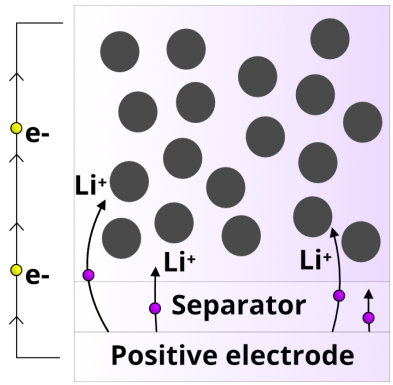

Figure 1.1: Two-dimensional illustration of a structural battery composite charge process. Li-ions migrate from the positive electrode into the carbon fibres, while electron transport occurs in the external circuit.

Studies on the effects of lithium insertion into carbon fibres, known as lithiation, have demonstrated that lithiation induces an anisotropic expansion of the fibre [13], [14]. Further investigations of carbon fibre lithiation conducted by Duan et al. reveal that fibre expansion can reach levels as high as 6.6 % in the radial direction and 0.89 % in the axial direction after full lithiation [14]. Moreover, it has been observed that the elastic moduli of the fibre are significantly affected, the transverse (i.e. radial direction) modulus increases by 107 %, while the longitudinal modulus experiences a decrease by 12 % after full lithiation. Consequently, operating the structural battery results in substantial changes in the internal stress state and stiffness properties of the composite [15]. The same coupling also leads to a response when a mechanical load is applied to lithiated (and partially lithiated) carbon fibres, resulting in a change in electric potential. This phenomenon, often referred to as stress-driven diffusion or the Piezo-Electro-Chemical Transducer effect (PECT), signifies the coupling of chemo-mechanical fields [16].
To assist in the development of structural batteries, computational models on

the battery cell level have been extensively addressed by Carlstedt et al., where they present fully coupled thermo-electro-chemo-mechanical frameworks [17]–[20]. These frameworks emphasize coupling of fields, such as the PECT effect. Furthermore, the models presented utilize linearized kinematics as well as linear reaction kinetics applied to a half-cell architecture, that is, the carbon fibre electrode against a lithium metal reference electrode.

Structural battery full cells have not been explored from a modelling viewpoint, i.e., the architecture shown in Figure 1.1 is yet to be analyzed. The active LFP particles inside the positive electrode come in sizes ranging from nanometer to micrometer in dimension. From a computational point of view, resolving the particles in the positive electrode and using direct numerical simulations on the battery cell level is not feasible for nano-sized particles [21]. To mitigate this issue, efforts have been made to develop homogeneous, macroscale models of electrodes and battery cells [22]–[26]. Redox reactions inside the positive electrode occur on the LFP particle / electrolyte interfaces, wherein the transport of neutral lithium atoms is governed by diffusion.
Adopting a homogeneous representation of the positive electrode leads to loss of information about the spatial position of the redox reactions and the active particle/electrolyte reaction kinetics. Redox reactions instead occur on an effective, simplified boundary. Furthermore, it should be noted that the averaged macroscopic properties as well as interface kinetics cannot be measured and must be determined numerically.

1.2 Research Scope

The aim of this thesis is to improve understanding of electrochemical and mechanical processes in structural battery electrodes and improve computational modelling techniques to better predict their electrochemical and mechanical behaviour. The emphasis is on the development of a reliable computational model for structural battery half and full cells, optimizing its parameters, assessing its sensitivity to various factors, and ensuring its ability to predict cell behaviour under different operating conditions. The research aims can be summarized in the following sub-goals;

- To understand the morphological changes and mechanical the response of carbon fibres during lithium-ion insertion.

- To develop a computational model that considers finite strains and lithium concentration-dependent fibre moduli to predict the mechanical behaviour of the structural electrode.
- To assess the significance of adopting the finite strain formulation in accurately representing the mechanical properties of the electrode and to investigate the internal stress states and effective expansion of the electrode caused by carbon fibre lithiation.
- To identify the material parameters used in the computational model to best fit the experimental charge-rest-discharge voltage profiles, aiming to improve the accuracy of the model.
- To quantify the influence of the material parameters on the overall performance of the cell and its ability to accurately predict voltage profile variations at different charge/discharge rates by sensitivity analysis.

CHAPTER 2

Summary of included papers

2.1 Paper A

Carl Larsson, Fredrik Larsson, Johanna Xu, Kenneth Runesson, Leif E. Asp
Effects of lithium insertion induced swelling of a structural battery negative electrode
Published in Composites Science and Technology,
vol. 244, no. 11, 2023.
 DOI: 10.1016/j.compscitech.2023.110299 .

In this paper, effects of lithiation of the carbon fibres on the mechanical properties and internal stress state of the negative electrode are studied. The method is outlined for analysis of features such as homogenized electrode stiffness and expansion, whereas the internal stress state analysis is carried out on the micro scale using a synthetical representative volume element (RVE). In particular, two extreme cases representing a fully constrained and an unconstrained electrode are considered. High internal stresses are expected for the fully constrained RVE, while lower stresses are expected for the unconstrained

RVE, where the RVE is allowed to expand freely. To properly represent geometrical change upon carbon fibre lithiation, finite deformation kinematics are adopted where a novel approach to homogeneous stress free expansion is presented. Results show a significant difference in the computed internal stress state and homogenized tangent stiffness when comparing the proposed finite strain model against the equivalent model using linear (small strain) kinematics. Moreover, the computed homogeneous expansion of the negative electrode as a function of state of lithiation exhibits similar trend to what is observed from experiments.

2.2 Paper B

Carl Larsson, Fredrik Larsson, Johanna Xu, Kenneth Runesson, Leif E. Asp
An Electro-Chemo-Mechanical Model for Analysis of Structural Battery Composite Full Cells
Manuscript.

In this paper, the coupled electro-chemo-mechanical modelling framework is extended to allow analysis of the structural battery full cell. For this purpose, a simplified, continuum representation of the positive electrode is adopted where redox reactions are restricted to a single interface. The occurring redox reactions are modelled using non-linear reaction kinetics pertinent to the Butler-Volmer relation for both positive and negative electrode interfaces. Mechanical fields are restricted to the negative electrode while the positive electrode is assumed to be stress free. Here, as a first step small strain kinematics is utilized. Measurement data is used as much as possible for the material parameters. The remaining material parameters, mainly applicable to the continuum positive electrode, are determined using optimization by comparing simulated charge-rest-discharge voltage profiles against experimental voltage profiles at two different rates. A sensitivity analysis is performed to quantify to what extent each optimized material parameter affect the simulated charge-rest-discharge voltage profile as well as the cost function. The results show that although the simplified representation of the positive electrode, the model is able to capture the general trend of the experimental voltage profiles for two different charge rates. Furthermore, the model is exemplified by simulating a future validation test case at a low charge rate where lower losses

related to rate of charge transfer are observed.

CHAPTER 3

Concluding remarks and outlook

This thesis covers some aspects of nonlinear modelling related to the structural battery application. In **Paper A**, we adopted finite deformation kinematics and studied the internal stress state as the carbon fibres expand. The numerical results show that finite deformation consideration is indeed needed to accurately predict the internal stress state as well as homogenized tangent stiffness at high carbon fibre lithiation levels. The highest simulated internal stress was approximately 200 MPa for the constrained RVE. The solid phase of the structural battery electrolyte matrix mainly consists of the material bisphenol A ethoxylate dimethacrylate. Such high stresses would most likely induce substantial development of plasticity and / or damage for these types of materials. The stress levels obtained are mainly a consequence of assuming a neo-Hookean material model, where the instantaneous stiffness increases with the level of strain.

In **Paper B** we extended the in-house modelling framework for analysis of the structural battery full cell, where the positive electrode was conceptualized as a (simplified) continuum while resolving the negative electrode on the micro scale. The coupled electro-chemo-mechanical model contains many material parameters, where measurement data was utilized as much as possible. The re-

maining material parameters, a majority pertaining to the positive electrode, were determined by optimizing the parameters against existing experimental voltage profiles. Using the proposed model and the calibration method, charge-rest-discharge voltage profiles can be simulated at any desired charge rate, which is further exemplified in the paper.
Future work will concern the following points;

i Determine and implement a constitutive model for the SBE motivated from experimental data. Explore possibilities of damage tolerance modelling of the SBE.

ii Extend the structural battery full cell model to include mechanical fields in the positive electrode.

iii Develop and implement a model for the positive electrode on the macroscale to consider the reactions related to the active particles inside the continuum.

iv Introduce finite deformation kinematics in the fully coupled electro-chemo-mechanical model for analysis of structural battery full cells.

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