



HAL
open science

Developments towards high energy density Li-batteries: new sulfide rocksalt cathode materials and improvement of lithium metal anode

Sebastien Martinet, Alex Cipolla, Benoit Chavillon, Benoit Mathieu, Celine Barchasz, Yagmur Celasun, David Peralta, Jean-François Colin

► To cite this version:

Sebastien Martinet, Alex Cipolla, Benoit Chavillon, Benoit Mathieu, Celine Barchasz, et al.. Developments towards high energy density Li-batteries: new sulfide rocksalt cathode materials and improvement of lithium metal anode. SIPS 2022, Nov 2022, Phuket, Thailand. cea-04248243

HAL Id: cea-04248243

<https://cea.hal.science/cea-04248243>

Submitted on 18 Oct 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Developments Towards High Energy Density Li-Batteries: New Sulfide Rocksalt Cathode Materials and Improvement of Lithium Metal Anode

S. Martinet, A. Cipolla, B. Chavillon, B. Mathieu, C. Barchasz,
Y. Celasun, A. Benayad, D. Peralta, J.F. Colin
Univ Grenoble Alpes, CEA LITEN DEHT
F-38000 Grenoble, France
sebastien.martinet@cea.fr

Li-Ion batteries are the technology of choice for most of today's applications, especially those demanding high energy densities. Large part of this success is due to intercalation electrodes, like graphite in the negative electrode and lamellar oxides in the positive electrode, which constitute a limit in term of energy density and power. Renewable energy and especially electric mobility demand a considerably higher energy density, which is unlikely to be met with the current technology. Therefore, investigating new materials to overcome these limits is fundamental. In this presentation, both cathode and anode developments will be considered.

In the first part, we will concentrate on overlithiated rock salts that are promising cathode materials for Li ion high energy applications. Despite the earlier results, these materials can offer much higher capacities (>250 mAh/g) than the stoichiometric compositions. This high capacity is associated to Li rich content that forms a good percolation network along the Li diffusion channels [1]. Lithium titanium sulfide (Li_2TiS_3), which has been reported by Sakuda *et al.* [2], demonstrated excellent capacity owing to the multielectron redox reactions. Upon cycling, more than two lithium ions were reversibly intercalated through the structure and the capacity reached 425 mAh/g. Besides these promising results, low electronic conductivity as well as poor cycling stability were also reported. To eliminate such disadvantages, doping or substitution can be an effective solution. Here, we propose new patented selenium substituted lithium titanium sulfide materials [3-4], which have been prepared by high energy ball milling. New materials showed better cycling stability than the current material. For a comparison, we will also provide a comprehensive study of these materials through fine characterization tools (XRD, SEM, EDX, voltammetry, XPS, ex situ and in situ XRD) in order to examine electrochemical and structural properties as well as the degradation mechanism.

In the second part, we will focus on Lithium metal that represents the ultimate candidate for the negative electrode, due to its high energy density and low potential. The major drawback of this technology is the formation of dendrites, which are structures that are formed on the surface of the metal electrode during the cycles of dissolution/precipitation. They cause loss of cyclable lithium, therefore they are responsible for the limited lifetime of this technology and may cause short-circuit and thus battery failures. Therefore, it is fundamental to understand the formation of these structures. The proposed model lies on the solid theoretical basis provided by Newman and Monroe [5], in which they proposed a steady-state model that considers the effect of the mechanical properties on the lithium deposition. On the other hand, the presented model is time-dependent and it adds the study of a pseudo-2D Solid Electrolyte Interface (SEI) component, starting from the work of Liu and Lu [6] in which both SEI creation, due to side reactions, and SEI fractures, due to change in geometry, are considered. Different from it, the effect of the mechanical properties of the SEI on the reaction kinetics is taken into account in this work. The surface of the electrode changes in shape due the electrodeposition of the lithium, which is proportional to the current on the surface, modeled with a modified Butler-Volmer kinetics. The model, with an example of results given in figure 2, is designed to be integrated with parameters that are found with a consistent set of experiments. Electrochemical Impedance Spectroscopy (EIS) and Atomic Force Microscopy (AFM) are conducted to find electrochemical and mechanical properties of the SEI. The proposed model has the goal of guiding the experiment in finding ways to avoid or curtail dendrites formation, being able to simulate the effect on dendrites growth depending on operative condition, SEI and electrolyte composition, electrode surface defect and coating.

References:

- [1] J. Lee, G. Ceder et al., *Science*, 343, 519-521 (2014)
- [2] A. Sakuda, *Sci. Rep.*, 4, 4883 (2014)
- [3] Y. Celasun, D. Peralta, J.F. Colin, S. Martinet. European Patent EP3626682 (2018)
- [4] Y. Celasun, D. Peralta, J.F. Colin, S. Martinet. European Patent EP3626681 (2018)
- [5] C. Monroe, J. Newman; *Journal of the Electrochemical Society* (2004)
- [6] G. Liu, W. Lu; *Journal of the Electrochemical Society* (2017)