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"Nanomaterials for Lithium-Ion Batteries: Fundamentals and Applications"

Edited by Rachid Yazami (Nanyang Technological University, Singapore), Pan Stanford Publishing Pte Ltd, USA, 2014, 448 pages, ISBN: 978-981-4316-40-8, £95.00, US$149.95

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"Nanomaterials for Lithium-Ion Batteries: Fundamentals and Applications" is edited by Rachid Yazami and is published by Pan Stanford Publishing Pte Ltd. The book covers the latest developments in new materials for lithium-ion batteries including examples of novel alloys, oxides and conversion materials for use as anodes and phosphates, high voltage spinels and layered oxides for use as cathodes. Composite structures incorporating reduced graphene oxide are considered along with thin films and nanowires. Emphasis is also placed on combining electrochemical test data with materials characterisation and detailed explanation of the mechanisms occurring.

Advanced Anode Materials

Chapter 1, 'Silicon Nanowire Electrodes for Lithium-Ion Battery Negative Electrodes' by Candace K. Chan (Arizona State University, USA) and Matthew T. McDowell and Yi Cui (Stanford University, USA), describes the advantages and challenges of nanostructured silicon as an anode material. The significantly enhanced capacity of silicon over conventional graphite electrodes is also associated with a huge volume change of ~300% on lithiation of silicon electrodes. The chapter describes how the preparation of thin layers or nanoscale structures can mitigate this volume change (**Figure 1**), but other aspects such as instability of the solid electrolyte interphase (SEI), cracking and detachment from the current collector with cycles are also important considerations. Methods to make silicon nanowires are discussed and the structural changes from the initial crystalline state to an amorphous structure after the first cycle are explained.

Chapter 2, 'Nanoscale Anodes of Silicon and Germanium for Lithium Batteries' by Jason Graetz and Feng Wang (Brookhaven National Laboratory, USA), extends the discussion to cover additional elements which can alloy with Li, then focuses on Si and Ge, both of which can achieve high capacity at a low voltage. Again the use of nanostructures is key to mitigate volume expansion issues and dissipate strain more readily during the expansion observed on lithiation of the material. Electrochemistry and cycling behaviour of thin films of Si and Ge are compared and the chapter concludes by commenting on the possible benefits of Si and Ge electrodes in solid state batteries and the requirement for materials engineering of composite structures to stop pulverisation and decrepitation with cycles.

Chapter 3, 'Nano-Electrochemical Approach for Improvement of Lithium-Tin Alloy Anode' by Tetsuya Osaka, Hiroki Nara and Hitomi Mukaibo (Waseda University, Japan), describes the promise of tin and tin alloys as Li storage materials. The approach of adding an inert spacer or scaffold element such as nickel to the tin is described, as Ni does not react with Li. Results

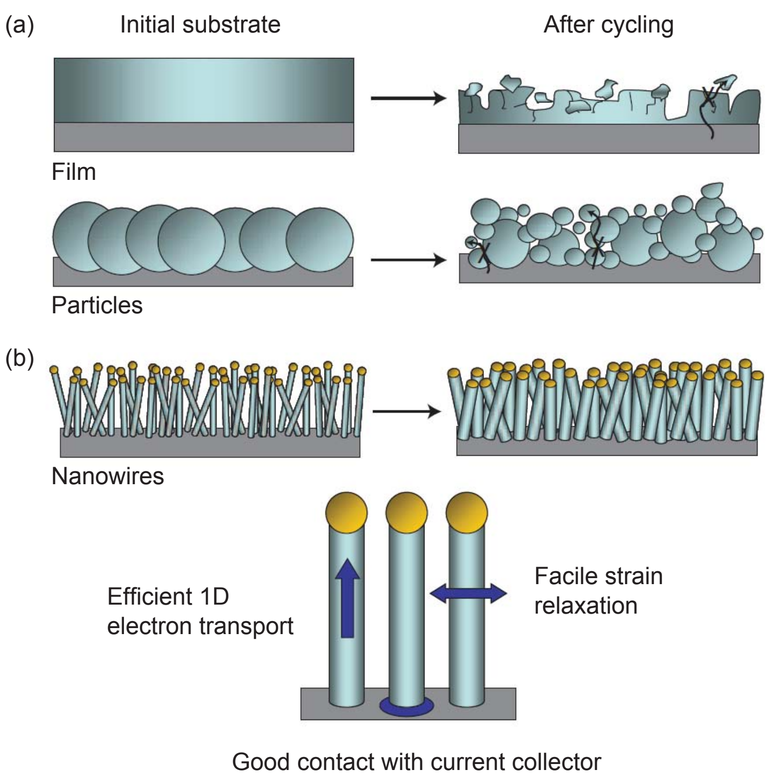

Fig. 1. Schematic of morphological changes that occur in Si during electrochemical cycling. (Reproduced with permission from (1). Copyright (2008) Nature Publishing Group)

of electrochemical testing and characterisation (X-ray diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction) are shown for films with various Sn:Ni ratios to illustrate the phases formed and the processes occurring; film composition Sn:Ni 62:38 showed the best performance. Calculations and *in situ* methods to measure stress on the electrode layer as a result of volume expansion are also described. Preparation of mesoporous Sn is also covered which shows improved cycling performance over denser Sn anodes.

Chapter 4, 'Alloy Electrode and Its Breakthrough Technology' by Kiyotaka Yasuda (Mitsui Mining and Smelting Co Ltd, Japan) provides a more historical perspective on the different types of anodes (Li metal and various alloy types) and also describes the different types of alloying reactions (internal displacement, phase separation and mixed reaction). The approach used by Mitsui in its SILX project on silicon based anodes is then discussed. Si particles are covered with a thin copper layer and formed into an electrode structure with ~30% cavity space. These features lead to good conductivity, prevent unwanted reaction of the electrolyte with Si and mitigate volume expansion issues, all of which lead to good performance and cyclability, especially at lower temperatures.

Chapter 5, 'Nanometer Anode Materials for Li-Ion Batteries' by Xuejie Huang and Hong Li (Chinese Academy of Sciences, China) describes the important features of anodes (low Li insertion and removal voltage, high capacity, low volume change, stability to electrolyte reactions, abundance and low cost) and also the various types of anode material (oxide, alloy, conversion) that are available. Examples of these different anode Li storage approaches are also provided, in particular the properties of transition metal oxide conversion materials. In such materials the metal oxide is converted to metal nanoparticles within a matrix of Li oxide by the lithiation process. The importance of achieving high mass and also high volumetric capacity for novel materials when comparing with currently used graphites is also emphasised.

Chapter 6, 'Lithium Reaction with Metal Nanofilms' by Rachid Yazami provides a concise and systematic description of the properties of different metal nanofilms during lithiation covering both non-alloying metals (where the only modes of Li storage are reaction with surface oxides and storage in micro cracks) and alloying metals (where incorporation of Li into the metal also takes place).

Cathode Materials

In Chapter 7, 'High-Rate Li-Ion Intercalation in Nanocrystalline Cathode Materials for High-Power Li-ion Batteries', Masashi Okubo (National Institute of Advanced Industrial Science and Technology, Japan) and Itaru Honma (Institute of Multidisciplinary Research for Advanced Materials, Japan) discuss the properties of lithium cobalt oxide ($LiCoO_2$) which is currently widely used as a lithium-ion battery cathode material. Theoretical and experimental aspects of this material are covered, such as correlation between lithium diffusion distances and high rate capability.

Chapters 8 and 9 cover an alternative cathode material, lithium iron phosphate ($LiFePO_4$), which is safer, lower cost and effective at high rates when made at nanosize and carbon coated (**Figure 2**). Chapter 8, '$LiFePO_4$: From an Insulator to a Robust Cathode Material' by Miran Gaberšček (National Institute of Chemistry, Slovenia) *et al*. is excellent, covering theoretical and experimental properties of $LiFePO_4$ from single crystals through to nanomaterials in electrode layers. The effect of size, models for different types of electrochemical contacting of active particles and network effects in cathode layers are all well explained. Chapter 9, 'Redox Reaction in Size-Controlled Li_xFePO_4 by Atsuo Yamada (The University of Tokyo, Japan) further elucidates the behaviour of $LiFePO_4$, covering redox reactions and the effect of particle size on the phase diagram; the adverse effects of exposure of $LiFePO_4$ to air which causes oxidation of surface Fe are also discussed.

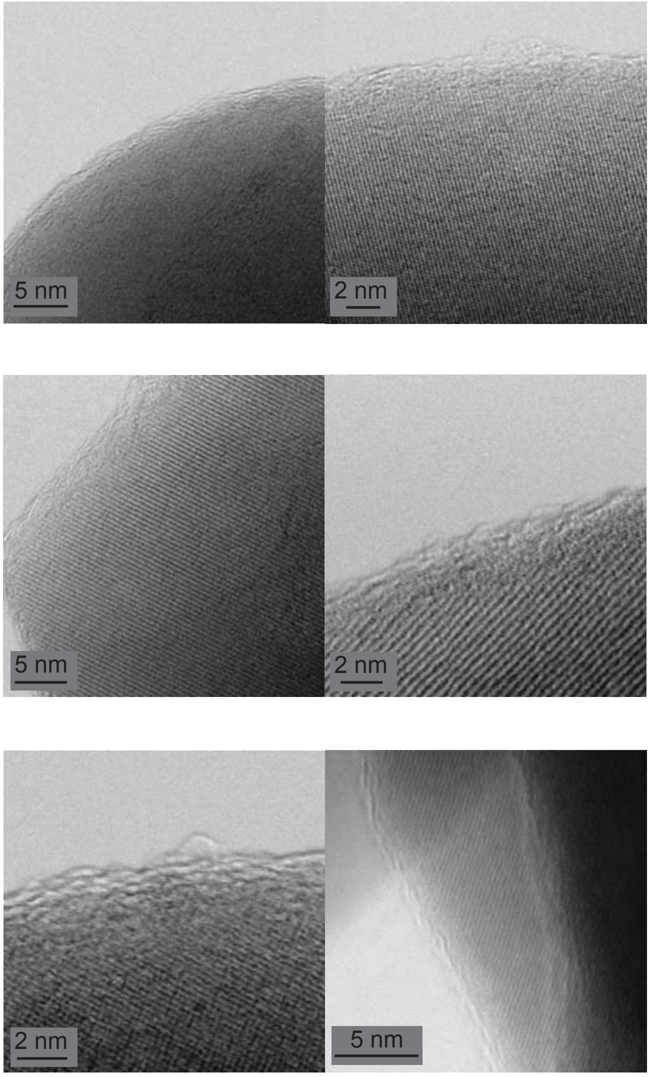

Fig. 2. TEM images of carbon coated $LiFePO_4$

Hybrid Materials and Practical Considerations

Chapter 10, 'Reduced Graphene Oxide–Based Hybrid Materials for High-Rate Lithium Ion Batteries' by Seong Min Bak, Hyun Kyung Kim, Sang Hoon Park and Kwang Bum Kim (Yonsei University, Republic of Korea) summarises the advantages and requirements for reduced graphene oxide (RGO) composite materials for both cathodes and anodes. These advantages include good conductivity and the ability to form small, well dispersed metal oxide particles on the RGO surface, preventing agglomeration of oxide particles and restacking of RGO and hence allowing good capacity and performance at high C-rates. Such materials may be made by microwave assisted hydrothermal synthesis and cathode (lithium manganese oxide ($LiMnO_4$)/RGO) and anode ($Li_4Ti_5O_{12}$/RGO) are both covered.

The final chapter of this book turns to more practical considerations and how the advanced materials already discussed can be effectively utilised to give high power and/or high energy in real cells. Chapter 11, 'High-Energy and High-Power Li-Ion Cells: Practical Interest/Limitation of Nanomaterials and Nanostructuration' is by S. Jouanneau, S. Patoux, Y. Reynier and S. Martinet (Commissariat à l'énergie atomique et aux énergies alternatives (CEA) Laboratory for Innovation in New Energy Technologies and Nanomaterials (LITEN), France). The advantages and challenges of a wide range of nanomaterials for cathodes, including olivine type lithium metal phosphates, layered oxides and high voltage spinels with various metal contents, are discussed. Experience with novel Si/C composite anodes and titanium oxides and titanates is also reviewed. The requirements for more stable high voltage electrolytes or appropriate additives to accompany these advanced materials are also considered along with binder and processing aspects. The chapter provides an overview of the potential usefulness of nanomaterials for battery applications.

Conclusions

This book provides a very useful introduction to the forthcoming advanced nanomaterials for lithium-ion anodes and cathodes. Benefits and disadvantages of a wide range of materials types are presented both in the context of fundamental materials properties and challenges of incorporating nanomaterials into practical electrodes and cells. Common themes within the chapters are the benefits of nanosizing materials in terms of shorter diffusion lengths, improved conductivity and better rate capability, but disadvantages such as low density and increased surface area leading to greater irreversible capacity and unstable SEI are also highlighted. Strategies to control volume expansion and limit material degradation with cycles *via* the preparation of composite materials and nanostructures, coatings or doping also feature across a wide number of the examples used.

Reference

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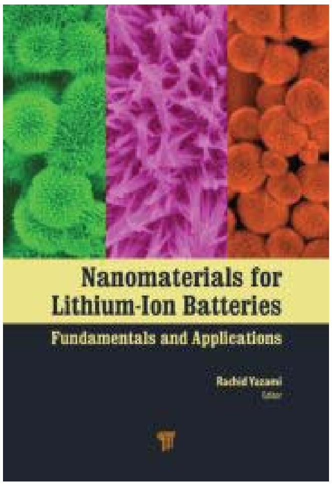

"Nanomaterials for Lithium-ion Batteries"

The Reviewer

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