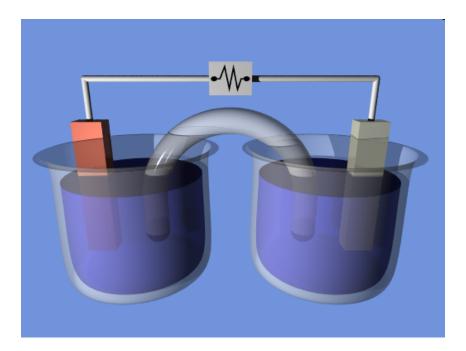
## Nanotechnology in Thin Film Batteries

# The Electrical Battery

- While a solar cell uses photons to generate electricity (flow of electrons), batteries use chemical reactions.
- Basically, a Voltaic cell containing two half cells are used.
- One cell contains the anode and the other the cathode. A conductive electrolyte connects the two cells in series.
- Most cells use two different electrolytes for the two halfcells and connect them with a porous separator that allows ion flow but not electrolyte mixing.



# Battery (cont.)

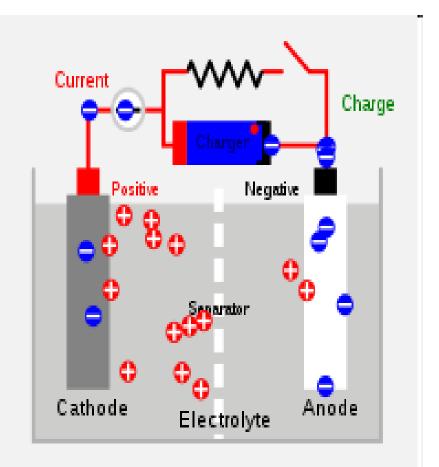
- A chemical reaction will occur in each half-cell between the electrode, electrolyte and possibly a catalyst.
- The reaction in the anode side produces an electron while the one in the cathode side requires one.
- The porous separator (a salt bridge or even a strip of paper soaked in potassium nitrate) acts as the conduit.
- Each half-cell has a characteristic voltage. The overall voltage provided by the cell is the difference between the two.

## **Disposable Batteries**

- Batteries can be classified in to disposable (primary) and rechargeable (secondary) types.
- Disposable batteries provide energy as long as the chemical reactants last.
- Alkaline batteries are the most common disposable batteries.
- They use the following half-reactions:
  - Zn (s) + 2OH<sup>-</sup> (aq)  $\rightarrow$  ZnO (s) + H<sub>2</sub>O (l) + 2e<sup>-</sup>
  - $2MnO_2 (s) + H_2O (I) + 2e^- → Mn_2O_3 (s) + 2OH^- (aq)$

## **Rechargeable Batteries**

- Rechargeable batteries are batteries where the chemical reaction can be reversed using an external current source such as a charger.
- Now the anode starts collecting electrons and the cathode provides them.



## **Types of Rechargeable Batteries**

- Lead Acid (car battery)
  - Oldest type of rechargeable battery.
  - Large power-weight ratio.
- NiCd
  - Can provide high surge current
- NiMH
  - Reasonable energy density
  - Memory effect
- Li-ion
  - High energy density
  - Can undergo many charge-discharge cycles

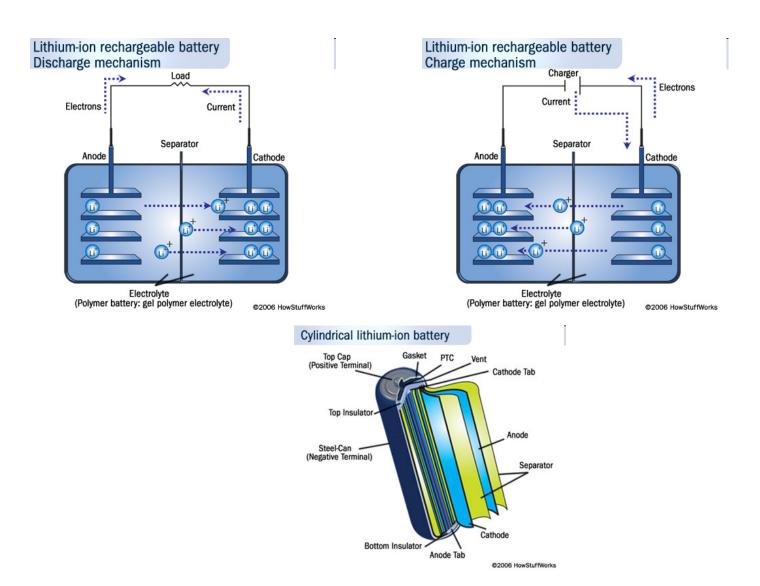
# **Li-ion Batteries**

- Li-ion batteries use Li ions moving between the anode and the cathode to generate electric current.
- The main components are the anode, the cathode and the electrolyte.
- The anode is mainly carbon and the cathode a metal oxide such as LiCoO<sub>2</sub> or LiMn<sub>2</sub>O<sub>4</sub>
- Both electrodes are capable of accepting Li ions (intercalation).
- The electrolyte is generally an organic solvent like ether.
- The half-reactions are:

 $\text{LiCoO}_2 \leftrightarrows \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$ 

 $x \operatorname{Li}^+ + x \operatorname{e}^- + 6 \operatorname{C} \leftrightarrows \operatorname{Li}_{\mathbf{x}} \operatorname{C}_6$ 

## Li-ion Batteries (cont.)

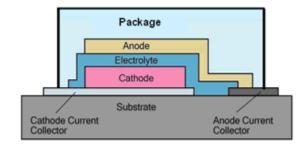


# Thin Film Batteries

- Unlike typical batteries, thin film batteries are all solid-state.
- In many cases they can be made flexible.
- They can be manufactured using normal thin film deposition techniques.
- Potential applications include:
  - RFID devices
  - Small sensors
  - Pacemakers
  - Neural stimulators
  - Drug delivery systems

## Thin Film Battery Design





Miniature thin film lithium battery on a ceramic substrate for use in an implantable medical device.

### Schematic layout of a thin film battery.

### Carbon nanocoatings on active materials for Li-ion batteries

R. Dominko<sup>a,\*</sup>, M. Gaberscek<sup>a</sup>, M. Bele<sup>a</sup>, D. Mihailovic<sup>b</sup>, J. Jamnik<sup>a</sup>

<sup>a</sup> National Institute of Chemistry, P.O.B. 660, SI-1001 Ljubljana, Slovenia <sup>b</sup> Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Available online 5 June 2006

#### Abstract

Carbon coatings were prepared on various submicrometre-sized particles that can be used as active materials in lithium rechargeable batteries. As a precursor citrate anion was used which, after carbonization at 500–600 °C, transforms into a uniform, several-nanometre-thick film that is tightly adhered to the surface of substrate particles. The coatings on  $Li_4Ti_5O_{12}$  and  $TiO_2$  increased significantly the average electron conductivity of cathode composite material, which resulted in a more than 100% increase of reversible capacity at a C/3 rate. Additionally, the coating on  $TiO_2$  prevented the gradual deterioration of reversible capacity of this material observed in absence of coating. In cases where due to temperature or atmosphere sensitivity of the substrate, carbon nanocoatings cannot be prepared, we propose the use of conductive polymers. A successful wiring using a sulphonated polyaniline is demonstrated on the example of MoS<sub>2</sub> nanotubes.

© 2006 Elsevier Ltd. All rights reserved.

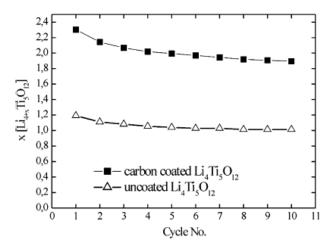


Fig. 3. Comparison of cycling behaviour of carbon-coated and uncoated  $Li_4Ti_5O_{12}$  active material. The material was cycled between 3 and 1 V vs.  $Li/Li^+$  at a C/3 rate.

### Spray deposition of steam treated and functionalized single-walled and multi-walled carbon nanotube films for supercapacitors

### Xin Zhao<sup>1,4</sup>, Bryan T T Chu<sup>1</sup>, Belén Ballesteros<sup>2</sup>, Weiliang Wang<sup>3</sup>, Colin Johnston<sup>1</sup>, John M Sykes<sup>1</sup> and Patrick S Grant<sup>1</sup>

<sup>1</sup> Department of Materials, Oxford University, Parks Road, Oxford OX1 3PH, UK

<sup>2</sup> Inorganic Chemistry Laboratory, Oxford University, South Parks Road,

Oxford OX1 3QR, UK

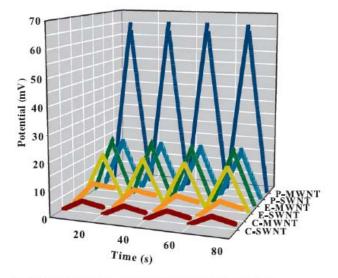
<sup>3</sup> Department of Engineering Science, Oxford University, Parks Road, Oxford OX1 3PJ, UK

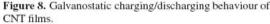
E-mail: xin.zhao@materials.ox.ac.uk

Received 16 October 2008, in final form 27 November 2008 Published 15 January 2009 Online at stacks.iop.org/Nano/20/065605

#### Abstract

Steam purified, carboxylic and ester functionalized single-walled carbon nanotube (SWNT) and multi-walled carbon nanotube (MWNT) films with homogeneous distribution and flexible control of thickness and area were fabricated on polymeric and metallic substrates using a modified spray deposition technique. By employing a pre-sprayed polyelectrolyte, the adhesion of the carbon nanotube (CNT) films to the substrates was significantly enhanced by electrostatic interaction. Carboxylic and ester functionalization improved electrochemical performance when immersed in 0.1 M H<sub>2</sub>SO<sub>4</sub> and the specific capacitance reached 155 and 77 F g<sup>-1</sup> for carboxylic functionalized SWNT and MWNT films respectively. Compared with existing techniques such as hot pressing, vacuum filtration and dip coating, the ambient pressure spray deposition technique is suggested as particularly well suited for preparing CNT films at large scale for applications including providing electrodes for electrochemical supercapacitors and paper batteries.





### Nano-wire networks of sulfur-polypyrrole composite cathode materials for rechargeable lithium batteries

Mingming Sun, Shichao Zhang\*, Tao Jiang, Lan Zhang, Jinhua Yu

School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, China

#### ARTICLE INFO

Article history: Received 5 August 2008 Received in revised form 6 September 2008 Accepted 10 September 2008 Available online 18 September 2008

Keywords: Sulfur Polypyrrole Network Composite

#### ABSTRACT

Polypyrrole (PPy) nanowire was synthesized through a surfactant mediated approach. The sulfur–polypyrrole (S–PPy) composite materials were prepared by heating the mixture of element sulfur and polypyrrole nanowire. The materials were characterized by FTIR, SEM. PPy with special morphology serves as conductive additive, distribution agent and absorbing agents, which effectively enhanced the electrochemical performance of sulfur. The initial discharge capacity of the active materials was 1222 mA h g<sup>-1</sup> the remaining capacity is 570 mA h g<sup>-1</sup> after 20th cycles.

© 2008 Elsevier B.V. All rights reserved.

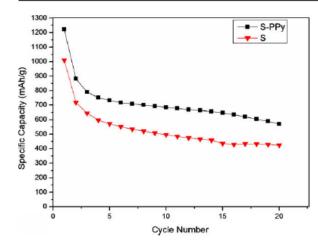


Fig. 4. Discharge capacities vs. cycle number for cathodes S-PPy composite and sulfur.

### Preparation and properties as positive electrodes of PANI–LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> nanocomposites

Eduardo Pérez-Cappe,<sup>a</sup> Yodalgis Mosqueda,<sup>a</sup> Ricardo Martínez,<sup>a</sup> Carlos Ricardo Milian,<sup>a</sup> Orlando Sánchez,<sup>b</sup> José A. Varela,<sup>c</sup> Alejandra Hortencia,<sup>c</sup> Eder Souza,<sup>c</sup> Pilar Aranda<sup>d</sup> and Eduardo Ruiz-Hitzky<sup>\*d</sup>

Received 5th March 2008, Accepted 5th June 2008 First published as an Advance Article on the web 9th July 2008 DOI: 10.1039/b803874k

PANI–LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> nanocomposite material with improved properties as positive electrode was prepared by a new synthesis method. In a first step, LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> mixed oxide in the form of a fine powder was dispersed in aniline and this suspension was sprayed on the surface of an aqueous solution of HCl and ammonium peroxodisulfate. The resulting PANI–LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> nanocomposite is spontaneously formed by polymerization of the aniline molecules present in the drops together with small particles of the oxide. This method induces the formation of nanocomposites showing a better distribution of the oxide particles in the polymer matrix than that observed in related PANI–LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> microcomposites prepared under ultrasound irradiation to disperse the oxide particles during PANI polymerization. Measurements of electrical conductivity and zeta potential, as well as structural characterization of PANI–LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> nanocomposites, reveal the existence of relatively strong interactions between the conducting polymer and the oxide particles. This feature determines higher values of the electrical conductivity (0.5 S cm<sup>-1</sup>) and of the average operative voltage (3.6 V), as well as of other technological parameters of the nanocomposite when it is used as the positive electrode of rechargeable lithium batteries, in comparison to those of the related microcomposite materials already reported.

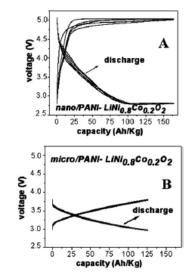


Fig. 8 The first five charge/discharge cycles (100  $\mu$ A) of lithium battery cells assembled with the *nano*/PANI–LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> (A) and *microl* PANI–LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> (B) composite materials as positive electrodes.

### Silicon nanowires for rechargeable lithium-ion battery anodes

Kuiqing Peng,<sup>1,2</sup> Jiansheng Jie,<sup>1</sup> Wenjun Zhang,<sup>1,3</sup> and Shuit-Tong Lee<sup>1,3,a)</sup> <sup>1</sup>Department of Physics and Materials Science, Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong SAR, People's Republic of China <sup>2</sup>Department of Materials Science and Engineering, Beijing Normal University, Beijing Radiation Center, Beijing Academy of Science and Technology, Beijing 100875, People's Republic of China <sup>3</sup>Nano-organic Photoelectronic Laboratory, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

(Received 5 February 2008; accepted 19 April 2008; published online 23 July 2008)

Large-area, wafer-scale silicon nanowire arrays prepared by metal-induced chemical etching are shown as promising scalable anode materials for rechargeable lithium battery. In addition to being low cost, large area, and easy to prepare, the electroless-etched silicon nanowires (SiNWs) have good conductivity and nanometer-scale rough surfaces; both features facilitate charge transport and insertion/extraction of Li ions. The electroless-etched SiNWs anode showed larger charge capacity and longer cycling stability than the conventional planar-polished Si wafer. © 2008 American Institute of Physics. [DOI: 10.1063/1.2929373]

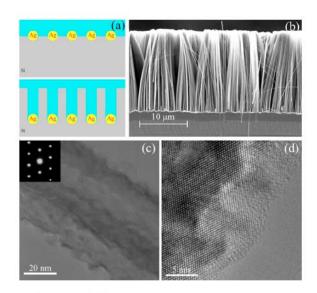
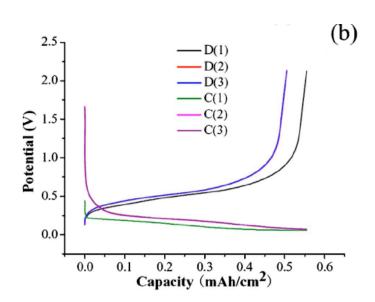


FIG. 1. (Color online) (a) Schematic formation of SiNWs via silver-induced etching. (b) Typical cross-sectional SEM image of SiNWs arrays. (c) TEM image of a segment of a single SiNW produced from Si(100) wafer. (d) HRTEM image of a SiNW, revealing the rough surface.





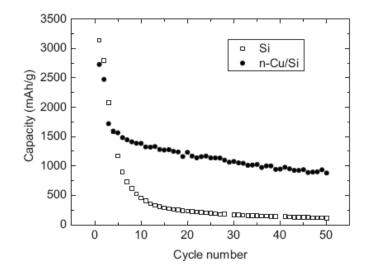
### Electrochemical Performances of Cu Nanodots Modified Amorphous Si Thin Films for Lithium–Ion Batteries

K.-F. Chiu,<sup>a,\*,z</sup> K. M. Lin,<sup>a</sup> H. C Lin,<sup>b</sup> C. H. Hsu,<sup>a</sup> C. C. Chen,<sup>a</sup> and D. T. Shieh<sup>c</sup>

<sup>a</sup>Department of Materials Science and Engineering, Feng Chia University, 407 Taichung, Taiwan <sup>b</sup>Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan <sup>c</sup>Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan

Amorphous Si thin films have been prepared using radio-frequency magnetron sputtering. Cu nanodots of 2–10 nm in diameter were sputter deposited on the surface of Si films. The Si films modified with Cu nanodots (n-Cu/Si) were used as anodes for lithium-ion batteries. The performances of the n-Cu/Si anodes with different thickness of Si films, 120 and 1000 nm, were characterized and compared. The Cu nanodots can greatly improve the cycling stability. The amount of capacity fading was 66% after 150 cycles for the thinner Si films (120 nm), and was over 90% after 50 cycles for thicker films (1000 nm). For the n-Cu/Si films, the amount of capacity fading was 33% for thin films and 45% for thicker films.

Manuscript submitted March 14, 2008; revised manuscript received May 13, 2008. Published July 8, 2008.



### Monoclinic $\beta$ -MoO<sub>3</sub> nanosheets produced by atmospheric microplasma: application to lithium-ion batteries

### Davide Mariotti<sup>1,2</sup>, Henrik Lindström<sup>3</sup>, Arumugam Chandra Bose<sup>1,4</sup> and Kostya (Ken) Ostrikov<sup>5,6</sup>

 <sup>1</sup> Nanoarchitectonics Research Centre, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan
<sup>2</sup> Department of Microelectronic Engineering, Rochester Institute of Technology, Rochester (NY), USA
<sup>3</sup> National Institute for Materials Science (NIMS), Tsukuba, Japan
<sup>4</sup> Department of Physics, National Institute of Technology, Tiruchirappali, India

<sup>5</sup> CSIRO Materials Science and Engineering, PO Box 218, Lindfield, NSW 2070, Australia

CSIRO Materiais Science and Engineering, PO Box 218, Lindheid, NSW 2070, Australia

<sup>6</sup> Plasma Nanoscience, The University of Sydney, Sydney, NSW 2006, Australia

E-mail: davide.mariotti@rit.edu

Received 7 July 2008, in final form 10 October 2008 Published 18 November 2008 Online at stacks.iop.org/Nano/19/495302

#### Abstract

Porous high surface area thin films of nanosheet-shaped monoclinic MoO<sub>3</sub> were deposited onto platinized Si substrates using patch antenna-based atmospheric microplasma processing. The films were characterized by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and electrochemical analysis. The electrochemical analysis shows original redox peaks and high charge capacity, and also indicates a reversible electrochemical behaviour particularly beneficial for applications in Li-ion batteries. SEM shows that the films are highly porous and consist of nanosheets 50–100 nm thick with surface dimensions in the micrometre range. HRTEM reveals that the MoO<sub>3</sub> nanosheets consist of the monoclinic beta phase of MoO<sub>3</sub>. These intricate nanoarchitectures made of monoclinic MoO<sub>3</sub> nanosheets have not been studied previously in the context of applications in Li-ion batteries and show superior structural and morphological features that enable effective insertion of Li ions.

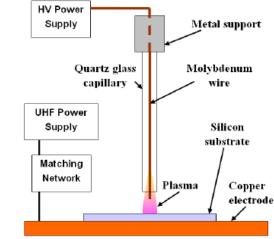


Figure 1. Experimental set-up used for the fabrication of MoO<sub>3</sub> nanosheets.

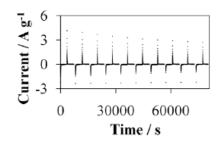


Figure 11. Consecutive charging/discharging cycles of  $MoO_3$ -ns deposited on platinized Si substrate. The potential was stepped from 3.7 to 1 V and from 1 to 3.7 V ten times. Each step lasted 1 h. The electrolyte was 1 M Li<sup>+</sup>.