



#### SPECIAL SYMPOSIUM TO HONOR

# MICHAEL THACKERAY

Casa de Convalescència Barcelona, March 10<sup>th</sup> 2013

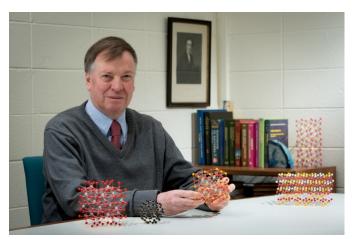
**Michael Thackeray** came to my laboratory at Oxford at the birth of oxide cathodes for the Li-ion battery. Peter Bruce was working with me on measurements of the Li<sup>+</sup> mobility in Li<sub>1-x</sub>CoO<sub>2</sub> and Bill David was a post-doctoral fellow who had just come to me from the Clarendon physics laboratory. Michael Thackeray had worked at the CSIRO in South Africa on the Zebra battery and he was one of the first to recognize the significance of an oxide cathode. Given the cost of a cobalt oxide, he had investigated a reversible insertion of Li into the spinel  $Fe_3O_4$ .

I didn't believe he could introduce an interstitial cation into a spinel lattice, so I suggested the Li was displacing the tetrahedral site iron to create a rock-salt phase. With Bill David, Michael proved me correct and also showed that for more than one inserted lithium, iron was being reversibly displaced from the spinel. This seminal experiment led to the immediate demonstration of reversible Li insertion into Li[Mn<sub>2</sub>]O<sub>4</sub> at 3 V versus Li. On his return to South Africa, Michael demonstrated a reversible Li extraction from Li[Mn<sub>2</sub>]O<sub>4</sub> at 4 V. The counter cation was thus shown to have a profound impact on the energy of the active redox couple. Problems with the Mn(III) ion led Michael to recognize the significance of the Ohzuku demonstration of reversible extraction of Li from Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> containing Ni(II) and Mn(IV). Also, his recognition of fast Li<sup>†</sup> transport in the spinel framework led him to patent the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel as a stable anode operation at 1.5 V vs. Li<sup>+</sup>/Li<sup>0</sup>. A second aspect of his work with Bill David was his recognition that Li-alloy displacement reaction can provide a high-capacity anode. Always an experimental solid-state chemist concerned with electrochemical energy storage, Michael Thackeray has provided outstanding leadership of the program at the Argonne National Laboratory that has led to the recent winning of the DOE HUB multi-million-dollar contract to develop batteries for the EV market and for storing electrical energy generated from alternative energy sources. May he and his group lead the way to a successful transition of our energy economy.

John B. Goodenough The University of Texas at Austin (USA)



# **BIOGRAPHY:**



**Michael Thackeray** is an Argonne Distinguished Fellow, senior scientist and group leader in the Electrochemical Energy Storage Department of the Chemical Sciences and Engineering Division at Argonne National Laboratory. He received his PhD from Cape Town University, South Africa in 1977 and was a post-doctoral fellow at Oxford University, UK. He worked as Manager of the Battery Unit at the Council of Scientific and Industrial Research (CSIR), South Africa before moving to Argonne in 1994. He is also

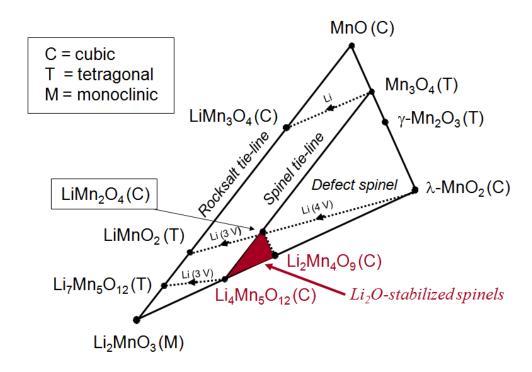
Director of the US Department of Energy's Energy Frontier Research Center - the Center for Electrical Energy Storage at Argonne.

**Dr. Thackeray's** research has resulted in 210 research publications. He contributed to the early concepts of high-temperature sodium-metal chloride ("Zebra") batteries and he has made a number of seminal contributions to the discovery and development of spinel-based and Li<sub>2</sub>MnO<sub>3</sub>-stabilized electrode materials used in the multi-billion dollar lithium-ion battery market. He holds 48 patents, several of which have been licensed to industry on an international scale.

Michael Thackeray is the recipient of several notable awards and honors, the most recent being the International Battery Association Yeager Award for life-long achievements in lithium battery electrode materials research and development (2011), U.S. Department of Energy R&D Award (2010), an R&D100 Award (2009), the Electrochemical Society Battery Division Research Award (2005) and the University of Chicago Distinguished Performance Medal (2003).

Michael is married to Lisa; they have three daughters, Caryn, Anna and Lara.





Steve Hackney (MTU): "Happy birthday to Mike Thackeray, one of the nicest people I have ever worked with. Although our birthdays come and go, the many important contributions Mike has made to solid state chemistry and electrode materials science are timeless"



# SCIENTIFIC PROGRAM



09:00

Bus Pick up at Hotel Catalonia Ramblas and transfer to Casa de Convalescència

#### 09.45 - 09:55 h WELCOME

Dr. Rosalind GUMMOW Dr. M. Rosa PALACÍN

## **OPENING LECTURE:**

09.55 –10.15 h Prof. Peter BRUCE

University of St. Andrews (UK)

### **Breathing Life into the Li-air Battery**

Going beyond the energy storage of Li-ion batteries will be important for the long-term needs of society. One option is the Li-air  $(O_2)$  battery, which promises, in theory, higher specific energy. The challenges facing the Li-air battery with aprotic electrolytes will be considered. Of particular importance is the electrolyte/cathode interface. The stability of the electrolyte and cathode will be discussed, as will the reactions at the interface, which should be  $2Li^+ + O_2 + 2e = Li_2O_2$ .

# MORNING SESSION – I

**Chair: Prof. STANLEY WHITTINGHAM** 

10.15 –10.35 h Dr. Jack VAUGHEY

**Dr. Chris JOHNSON** 

Argonne National Laboratory (US)

### Our nearly 20 years of Battery Research with Mike Thackeray at Argonne

Over the past 20 years, the search for new Li-ion battery materials at Argonne has produced an array of new lithium-ion anodes and cathodes that have attracted worldwide attention. Intermetallic insertion compounds, LTO and LMO spinel, lithium vanadium oxides, manganese oxides, lithium iron oxides and Li & Mn-rich 'layered\*layered' oxides have been studied as electrodes in Li batteries. A discussion of these systems will be provided along with a perspective of Mike's tenure at Argonne.



#### 10:35 – 10:55 h Prof. Jean-Marie TARASCON

Université de Picardie Jules Verne (France)

### The Long and Winding Road to Optimize LiMn<sub>2</sub>O<sub>4</sub> electrodes

More than 30 years have passed since J.C.Hunter reported the first evidence of de-inserting Li from LiMn<sub>2</sub>O<sub>4</sub>. This finding rapidly drove the battery community interest for this spinel phase with M. Thackeray being the most active and prolific player since then. Trying to turn this material into a practical electrode was also one of my objectives back to 1990. Since that time Mike and I have been friendly competitors, the best situation to keep science moving ahead. During this lecture will be retraced the key steps of the scientific venture necessary to master the physical chemistry of LiMn<sub>2</sub>O<sub>4</sub> leading to the development of the rechargeable Li-ion LiMn<sub>2</sub>O<sub>4</sub>/C technology with emphasis on Mike's contribution.

## 10:55 – 11:15 Prof. Kristina EDSTRÖM

Uppsala University (Sweden)

#### Model studies of Cu<sub>2</sub>Sb inspired by Mike

Many different parameters are important for the success of a material to be used as an electrode material in a Li-ion battery. Cu<sub>2</sub>Sb is one example of a negative electrode material is used as a model system for studying how details in synthesis and structure can be tuned for maximum cyclability despite the fact that large volume changes occur during cycling. In this presentation some of Mike's contributions to the understanding of intermetallics for both two-dimensional and complex tree-dimensional structures and substrates will be discussed. A special emphasis will be on the mechanisms for lithium ion insertion in the material

#### 11:15 - 11:45 Coffee-Break



## **MORNING SESSION – II**

**Chair: Prof. PETER BRUCE** 

11:45 – 12:05 **Prof. Stan WHITTINGHAM** 

SUNY Binghamton (US)

#### **Molten through Intercalation to Conversion Batteries**

The first rechargeable alkali batteries used molten electrodes — the first commercially successfully batteries used intercalation reactions — and today conversion reactions, initially for the anode are coming into vogue. The concepts have bubbled-up from the US, UK and South Africa with help from Mike Thackeray all along the way.

12:05 – 12:25 **Dr. Rosalind GUMMOW** 

James Cook University (Australia)

# Supercharged: Battery Technology in Mike Thackeray's Group at the CSIR, South Africa 1988-1994

During the late 1980's and early 1990's I was fortunate to be a part of Mike Thackeray's Battery Technology Group at the CSIR in Pretoria. Under Mike's leadership the group was able to make significant contributions in many diverse areas of battery technology and especially in lithium-ion battery cathode development. In this talk I will share personal memories of my time at the CSIR South Africa and some of the developments that were made at that time.

#### 12:25 – 12:45 **Prof. Kenneth OZOEMENA**

Council for Scientific and Industrial Research (CSIR) - (South Africa)

# The use of microwave irradiation in controlling the Mn<sup>3+</sup> concentration and electrochemical performance of high-voltage LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> spinel

LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> spinel which has been receiving major research attention as electrode material because of its high operating voltage ( $^{\sim}$  4.8 V) and the high intrinsic rate capability. It is well established that the electrochemical performance of LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> is intricately linked to the Mn<sup>3+</sup> content, degree of disorder, and Li<sub>y</sub>Ni<sub>1-y</sub>O impurity. In this presentation, we introduce microwave strategy as a viable strategy to control the Mn<sup>3+</sup> concentration and electrochemical performance of LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> spinel.



#### 12:45 – 13:05 **Prof. Martin WINTER**

Münster Universität (Germany)

# How do reactions at the anode/electrolyte interface deteriorate cathode performance?

Today, it is common knowledge, that materials science in the field of electrochemical storage has to follow a system approach as the interactions between active materials, the electrolyte, the separator and various inactive materials (binder, current collector, conductive fillers, cell-housing, etc.) are of similar or even higher importance as the properties and performance parameters of the individual materials only. In particular, for lithium and lithium-ion batteries, it is widely accepted that the electrolyte interacts and reacts with the electrodes. We report how reactions at a the anode (involving electrolyte decomposition and solid electrolyte interphase formation), affect the performance of a LiCoO<sub>2</sub> (LCO) cathode and the full lithium-ion cell during cycling. We discuss effects of the SEI-forming electrolyte additive vinylene carbonate (VC) and the influence of graphite anodes with different surface areas on the cycling stability and end of charge potentials of the LCO cathode.

#### 13:15 – 15:00 Lunch time and group pictures

#### AFTERNOON SESSION – I

Chair: Dr. ROSALIND GUMMOW

15:00 – 15:20 **Dr. Steve LEVINE** 

Georgetown University (US)

The Little-Known Literary Side of Batteries

15:20 – 15:40 **Prof. Clare GREY** 

University of Cambridge (UK) - Stony Brook University (USA)

# Spinels, Olivine and Layered Materials – In and Ex-situ NMR Studies of Local Order

This talk will describe recent efforts to understand cation ordering and dynamics in lithium electrode materials focusing on the combined use of NMR and DFT based methods to help identify local structures, focusing on some MMT-inspired systems and chemistries.



15:40 – 16:00 **Prof. Bill DAVID** 

ISIS, Rutherford Laboratory (UK) - Oxford University (UK)

#### Lithium pathways

Mike arrived in the JBG group in Oxford in 1981 shortly after I had started as a post-doc with John working on Nasicon-related materials; and it was Mike who persuaded me to move from sodium to follow the lithium pathway. After briefly reminiscing about our more serendipitous Oxford experiments, I will describe some of my recent work on lightweight hydrogen storage materials where insights from the 1980 Oxford days have helped explain mechanisms of hydrogen reversibility. Lithium diffusion pathways turn out to be crucial in these systems and this has led to our development of novel non-equilibrium DFT-based molecular dynamics algorithms which may help bring insights into long-timescale diffusion mechanisms in lithium battery systems.

16:00 – 16:20 **Dr. Robert KOSTECKI** 

Lawrence Berkeley National Lab (US)

Near-Field Optical Imaging of Interfaces and Interphases in Battery Materials

Development of new innovative experimental approaches and enabling methodologies to understand the function and mechanism of operation of materials and electrodes for Li-ion batteries is critical for electrification of transportation. The advent of femtosecond (fs) lasers and near-field optical methods during the past decades has led to the development of new advanced techniques for chemical analysis This presentation provides an overview of novel in situ and ex situ experimental approaches aimed at probing battery materials and electrodes in electrical storage systems at an atom, molecular or nanoparticulate level.

16:20 – 16:50 Coffee-Break



## AFTERNOON SESSION – II

**Chair: Prof. BILL DAVID** 

16:50 – 17:10 **Dr. Karim ZHAGIB** 

**HYDROQUEBEC** (Canada)

#### **HQ-CSIR LTO for Energy Storage and Green Transportation**

LTO is used for negative electrode for LMO, LFP and 5 V batteries. LTO gives safety and fast charge battery (1 minute) charge. It is a good candidate for energy storage, EV and E-bus

17:10 – 17:30 **Prof. Doron AURBACH** 

Bar Ilan University (Israel)

# Adventures with the high capacity cathode materials invented by Michael Thackeray et al.

The  $Li_2MnO_3$ - $Li[MnNiCo]O_2$  cathode materials developed at ANL are in the focus of intensive studies throughout the world, since they can be considered as the horizon of Li ion battery technology in terms of energy density. In this talk we will share with you results from our own studies at BIU. Rigorous electrochemical, spectroscopic, diffractometric and microscopic measurements were carried out, demonstrated very promising capacity and reasonable rate capability and safety features, revealed interesting structural changes and left question marks re: cycling stability.

17:30 – 18:00 **Dr. Jeffrey P. CHAMBERLAIN** 

Argonne National Laboratory (US)

**Dr. Emilio BUNEL** 

Argonne National Laboratory (US)

Use-Inspired Basic Research – A Trademark of Mike Thackeray's Career and its Impact on Argonne's Battery R&D Program

Most material researchers tend to either focus on scientifically interesting phenomena, giving little thought to practical applications, or they focus on developing new or refined materials for industrial applications, without totally



understanding the basic science associated with the new materials. Few researchers possess the unique ability to conduct use-inspired basic materials research of the type conducted by Mike Thackeray. This aspect of his career and its impact on Argonne's battery program will be discussed.

18:00 – 18:10 **Dr. Michael M. THACKERAY** 

Argonne National Laboratory (US)

**Grateful Reflections** 

18:10 Prof. Bor Yann LIAW

**Prof. Yang SHAO-HORN** 

**Closing remarks** 

18:40 Bus Pick up and transfer to Hotel Catalonia Ramblas

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