VTT SYMPOSIUM 268

# EICOON Workshop and Summer School

## Nanomaterial Issues in Electrochemical Energy Conversion: Fuel Cells, Batteries, Supercapacitors

VTT SYMPOSIUM 268

**Keywords:** nanomaterial, electrochemistry, fuel cell, battery, supercapacitor

# Eicoon Workshop and Summer School

# Nanomaterial Issues in Electrochemical Energy Conversion:

## Fuel Cells, Batteries, Supercapacitors

**June 13–17, 2011**

**Technopolis Innopoli 1**
**Tekniikantie 12, Espoo, Finland**

**Edited by**
**Annemari Kuokka-Ihalainen, VTT**
**Pertti Kauranen, VTT**

**Organised by**
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# Preface

In a globalized world energy is a decisive factor for the further development and economic and social well being of the nations and stability in the different world regions. Materials science and research has in the past significantly contributed to solving issues in sustainable energy technologies. To bring about advancement and improvements in energy technologies and to address sustainability, research in nano-materials is expected to contribute significantly to solutions in a highly competitive and increasingly globalize world. Such research will inevitably have to be coordinated at European level but also internationally. In Europe, materials researchers cooperate increasingly in EU funded projects and bilaterally with non-European countries. The EU has concluded S&T agreements and implementation arrangements with India. It foresees the coordination and the execution of joint projects. The EICOON project addresses the strategic assessment including synergy analysis of nano-materials research needs in the EU and India. It establishes and communicates to DG RTD and DST the mutual interests and the topics for future coordinated calls to enable the decision & policy makers and the funding bodies to make better informed decisions and to better select the implementation mechanisms and instruments. Beside the assessment, EICOON also addresses the dissemination of the “nano-materials research acquis” in the field by organization of events. Finally, it will bring together researchers for future research collaboration, to exchange ideas for joint projects and to inform each other on their core competencies & expertise. The project aims at the generation and enhancement of knowledge in materials science and research especially nano-materials applied to sustainable energy technologies. It also aims to increase the deployment of these materials in the technologies in both regions.

The EICOON workshop and school “Nanomaterial issues in electrochemical energy conversion: fuel cells, batteries and supercapacitors” is part of project organization of scientific seminars and thematic summer schools. All the speakers, poster presenters, laboratory tour hosts and members of the international and local organizing committee as well as the scientific committee are acknowledged for their invaluable contributions to the success of the workshop and school. Finally, project funding by EU under the contract 233466 and workshop funding by the industrial sponsors are gratefully acknowledged.

I wish you welcome to Espoo and hope that it will become an unforgettable week for all of us.

Dr. Pertti Kauranen
Chairman of the organizing committee

## Scientific Committee for the EICOON School

Dr. Pertti Kauranen, VTT, Finland
Prof. Maarit Karppinen, Aalto University, Finland
Dr. Carina Lagergren, Royal Institute of Technology, Sweden
Prof. Svein Sunde, Norwegian University of Science and Technology, Norway
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Ms. Annemari Kuokka-Ihalainen, VTT, Finland
Ms. Eeva Honkajuuri, VTT, Finland

## EICOON Project Partners

India

- Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore
  Prof. C.N.R. Rao, Prof. S.M. Shivaprasad, Dr. M. Aruna
- Indian Institute of Technology Delhi, New Delhi
  Prof. B.R. Mehta, Dr. Mandeep Singh
- S.N. Bose National Center for Basic Sciences, Kolkata
  Dr. A.K. Raychaudhuri, Dr. Sugata Mukherjee
- Indian Institute of Technology Kharagpur, Kharagpur
  Prof. I. Manna, Dr. J.D. Majumdar
- Confederation of Indian Industries, Chennai
  Mr. G.K. Moinudeen, Mr. T. Hariharan
- National Chemical Laboratory, Pune
  Dr. S. Sivarom, Dr. V.K. Pillai, Dr. V.V. Ranade

Europe

- MESA+ Institute of Technology, The Netherlands
  Prof. D.H.A. Blank, Dr. M. Huijben, Dr. D.C. Kitty Nijmeijer
- JRC Institute of Energy, The Netherlands
  Prof. G. Tsotridis, Dr. T. Malkow
- Sociedade Portuguesa de Inovacao, Portugal
  Dr. Miguel Santos
- VTT Technical Research Center, Finland
  Dr. Pertti Kauranen
- Institute of Nanotechnology, Scotland
  Dr. A. Stewart
- ENEA Cassacia Research Centre, Italy
  Dr. Dario Della Sala

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Session II

# Programme

**Eicoon Workshop and Summer School**
Nanomaterial Issues in Electrochemical Energy Conversion:
Fuel Cells, Batteries, Supercapacitors

**Dates** 13–14 June 2011 Workshop
15–17 June 2011 Summer School

**Location** Technopolis Innopoli 1, Tekniikantie 12, Espoo, Finland

## Workshop 13 June 2011

| | |
|---|---|
| 08.30 | **Registration** |
| 09.30 | **Welcome**<br>Prof. Anne Ritschkoff, VTT, Finland |
| | **Introduction to EICOON**<br>Prof. Georgios Tsotridis, Joint Research Centre, Petten, The Netherlands |
| | **Inaugural addresses** |
| 10.00 | **On the EU SET-Plan and EERA with perspectives on nanomaterials for electrochemical energy converters**<br>Prof. Henrik Bidslev, Aarhus University, Denmark |
| 10.30 | **Thin Film and Nanomaterial based solar cell technologies**<br>Prof. K.L. Chopra, Indian Institute of Technology, New Delhi, India |
| 11.00 | Coffee |
| | **Keynote lectures** |
| 11.30 | **Nanoscience and Nanotechnology in Low Temperature Fuel Cell Research**<br>Prof. Jürgen Behm, University of Ulm, Germany |
| 12.15 | **Fabrication and Designing of New Electrolyte for SOFC**<br>Prof. Indranil Manna, Director of Central Glass and Ceramic Research Institute (under CSIR), India |
| 13.00 | Lunch |
| 14.00 | **Nanomaterials in Commercial PEM and DMFC Fuel Cell Applications**<br>Mr. Steen Yde-Andersen, IRD Fuel Cells A/S, Svendborg, Denmark |

| | |
|---|---|
| 14.30 | **Some advances in nanomaterials for PEMFC**<br>Prof. Deborah Jones, University of Montpellier, France |
| 15.00 | Coffee |
| 15.30 | **Nanomaterials in SOFC manufacturing. Benefits and disadvantages**<br>Dr. Johan Subbi, National Institute of Chemical Physics and Biophysics, Estonia |
| 16.00 | **Nanostructural engineering of SOFC fuel electrodes**<br>Prof. John Irvine, University of St. Andrews, UK |
| 19.30 | Dinner |

## Workshop 14 June 2011

| | |
|---|---|
| 09.00 | **Advantages and drawbacks of nanomaterials for battery applications**<br>Dr. Christian Jordy, Saft Batteries, France |
| 09.40 | **Synthesis of SiO nanoparticles for Li-ion batteries**<br>Dr. Ari Auvinen, VTT, Espoo Finland |
| 10.20 | Coffee |
| 10.50 | **Nanomaterials for Supercapacitors: Enhancement and novel properties**<br>Dr. Pritesh Hiralal, Nokia Research Centre, Cambridge, UK |
| 11.30 | **Supercapacitors: materials, performances and applications**<br>Dr. Mario Conte, ENEA Cassacia Research Centre, Rome, Italy |
| 12.10 | **Nanostructured Materials for Electrochemical Energy Systems**<br>Prof. S. Sampath, Indian Institute of Science, Bangalore, India |
| 12.50 | Lunch |
| 13.50 | **ALD from emerging applications to industrial production**<br>Dr. Matti Putkonen, Beneq Ltd. |
| 14.10 | **The outcome of the previous EICOON workshop**<br>Dr. Thomas Malkow, Joint Research Centre, Petten, The Netherlands |
| 14.40 | Coffee |
| 15.10 | Panel discussion |
| 16.30 | Workshop summary |
| 19.30 | Dinner for lecturers |

## Summer School 15 June 2011

| | |
|---|---|
| 08.30 | **Registration** |
| 09.00 | **Welcome**<br>Dr. Pertti Kauranen, VTT, Finland |
| 09.10 | **Introduction to the EICOON project**<br>Prof. Georgios Tsotridis, Joint Research Centre, Petten, The Netherlands |
| | **Plenary lecture** |
| 09.20 | **Hybrid ultracapacitors and their applications**<br>Prof. A.K. Shukla, Indian Institute of Science, Bangalore, India |
| 10.00 | Coffee |
| 10.30 | **Direct alcohol fuel cell developments based on different low temperature fuel cell technologies**<br>Dr. Carsten Cremers, Fraunhofer Institute of Chemical Technology, Germany |
| 11.10 | **Durable Platinum catalyst on CNT supports for PEMFCs**<br>Prof. A.M. Kannan, Arizona State University, Pheonix, USA |
| 11.50 | **Surface Species and Product Distribution in the Electrooxidation of Small Organic Molecules**<br>Prof. Jürgen Behm, University of Ulm, Germany |
| 12.30 | Discussion |
| 12.40 | Lunch |
| 13.40 | **Materials and design challenges in solid oxide fuel cell**<br>Prof. Indranil Manna, Director of Central Glass and Ceramic Research Institute (under CSIR), Kolkata, India |
| 14.20 | **Printed power sources based on renewable materials**<br>Dr. Sanna Carlsson, VTT, Finland |
| 15.00 | Discussion |
| 15.10 | Coffee |
| 15.40 | **Poster session 1: Fuel cells** |
| 16.30 | EICOON project meeting |
| 19.30 | Dinner for lecturers |

## Summer School 16 June 2011

| | |
|---|---|
| 09.00 | **Coatings for Batteries and Supercapacitors**<br>Prof. Jyotsna Dutta Majumdar, Indian Institute of Technology, India |
| 09.40 | **Application of functionalized carbon nanotubes for polymer electrolyte fuel cells**<br>Dr. Vijaymohanan Pillai, CSIR-Central Electrochemical Research Institute, India |
| 10.20 | Coffee |
| 10.50 | **Carbon nanomaterials as support of Pt-based electrocatalysts for PEMFC electrodes**<br>Dr. Rosella Giorgi, ENEA Cassacia Research Centre, Rome, Italy |
| 11.30 | **Electronic structure and properties of carbon and boron nitride based nanomaterials**<br>Prof. Sugata Mukherjee, S.N. Bose National Centre for Basic Science, India |
| 12.10 | **Floating catalyst synthesis and direct dry deposition of SWCNTs for thin film applications**<br>Prof. Esko Kauppinen, Aalto University, Espoo, Finland |
| 12.50 | Lunch |
| 13.50 | **Poster session 2: Batteries and basic nanoscience** |
| 14.50 | **Lab tours:**<br>1. SOFC / PEMFC — VTT<br>2. Batteries — VTT / Aalto University<br>3. Nanocarbons — Aalto University |
| 19.00 | Dinner for students and lecturers |

## Summer School 17 June 2011

| | |
|---|---|
| 09.00 | **Emerging issues on health effects of engineered nanomaterials**<br>Dr. Kai Savolainen, Finnish Institute for Occupational Health, Finland |
| 09.40 | **Carbon nanomaterials for electrochemical capacitors**<br>Dr. Rüdiger Kötz, Paul Scherrer Institute, Villigen, Switzerland |
| 10.20 | Coffee |
| 10.50 | **Enhancing the hydrogenation properties of Pd and Pd alloy nanoparticles**<br>Prof. B.R. Mehta, Indian Institute of Technology, New Delhi, India |
| 11.30 | **Gas phase synthesis of anode materials for Li-ion batteries**<br>Prof. Jorma Jokiniemi, VTT, Finland |
| 12.10 | **Theoretical study of binding and desorption of hydrogen on doped magnesium hydride and light metal decorated metal-organic framework**<br>Prof. Sourav Pal, National Chemical Laboratory, Pune, India |
| 12.50 | Lunch |
| 13.50 | Best poster prices |
| 14.20 | Closing discussion |

# CV’S OF
THE SPEAKERS

## Dr. Henrik Bindslev

**Vice Dean for research, Aarhus University, Faculty of Science and Technology**
**Chairman of the European Energy Research Alliance**

Following his PhD in Plasma Physics for University of Oxford, Henrik engaged in fusion energy research at the European fusion research centre JET, and subsequently at the Dutch research centre FOM and later at Risø National laboratory. 2007 till 2011 as Director of Risø National Laboratory for Sustainable Energy, DTU, Henrik engaged the full range of sustainable energy research topics, initiating among others batteries research at Risø DTU. 2010 Henrik was elected Chairman of the European energy Research Alliance, which today conducts 7 Joint Programmes with more than 85 participating research organisation.

## Prof. K.L. Chopra

**Senior Professor and Former Director, IIT Kharagpur**

Prof. (Dr.) Kasturi Chopra has made pioneering contributions to the science and technology of thin-films for five decades. In the area of thin-film solar cells, development of chemical bath deposition process for CdS films (used universally by thin-film solar cell industries worldover), deposition of conducting ZnO films, development of Cu2S/ CdS and Cu-In-S thin film solar cells are some of the pioneering contributions of Prof Chopra and his Thin Film Laboratory, IIT Delhi research group. Author of over 430 research publications and several books which include the well-known treatise “Thin Film Phenomena”, “Thin Film Solar Cells” and “Thin Film Device Applications”, he is an Associate Editor of the Elsevier Journal “Solar Energy Materials & Solar Cells”.

## Prof. Dr. Rolf Jürgen Behm

**Professor of Physical Chemistry at Universität Ulm**

The research interest of the Behm group focuses on the mechanistic understanding of reactions and processes at surfaces and interfaces on an atomic/ molecular scale, with special emphasis on correlations between structure and reactivity. The work reaches from studies on structurally well defined surfaces and interfaces under idealized conditions (surface structure, surface reactions, metal deposition, reactivity of bimetallic surfaces) via studies on nanostructured surfaces/interfaces (e.g. on transport effects) to studies employing realistic materials (supported catalysts) and reaction conditions (Heterogeneous Catalysis, Electrocatalysis). In recent years, the work concentrated on reactions related to Low Temperature Fuel Cells (electrocatalytic reactions and fuel gas processing (Heterogeneous Catalysis).

## Prof. Indranil Manna

**Central Glass and Ceramic Research Institute, Kolkata**

Professor Indranil Manna is currently the Director, Central Glass and Ceramic Research Institute, Kolkata (a CSIR Unit) and the INAE Visvesvarya Chair Professor (on lien from IIT, Kharagpur). His research interest concerns structure-property correlation and modeling in nanometric solids, laser/plasma assisted surface engineering, fuel cell, sensors, nano-fluid and bainitic steel. Prof Manna has published over 225 papers, guided 15 doctoral students and received several awards including Humboldt and DAAD Fellowship, INSA Young Scientist Award, Young Metallurgist and Metallurgist of the Year award of the Ministry of Steel, Platinum Jubilee Medal of Indian Science Congress, GD Birla Medal of Indian Institute of Metals, etc. He is a Fellow of all Science (INSA, IAS, NASI) and Engineering (INAE, IE(I), IIM) academies in India.

## Steen Yde-Andersen

**CEO**
**IRD Fuel Cells, LLC**

Steen Yde-Andersen is graduated from Copenhagen University with a M.S. in Chemistry and has been involved with fuel cell, super capacitor and battery research and development since 1982 and as such participated or coordinated many national and international research projects both public and private funded. Steen Yde-Andersen has as a results of this been involved in starting or founding several companies within the area of batteries and fuel cells as in 2009 as General Manager for IRD Fuel Cells, LLC. Steen Yde-Andersen joined IRD Fuel Cells A/S in 1998 as Manager of R&D at IRD.

## Dr. Deborah Jones

**Full Senior Research Scientist**
**CNRS Montpellier**

Deborah J. Jones is Director of Research at CNRS and heads the laboratory for “Aggregates, Interfaces and Materials for Energy” at the Institute for Molecular Chemistry and Materials at Montpellier University, France, and the University’s research and Masters interdisciplinary programme on “Energy”. Deborah Jones has co-authored 180 peer-reviewed journal articles and ten review articles on synthesis and characterisation of electrochemically active materials, in particular for energy conversion and storage, ion-exchange, insertion and intercalation, hydrogen bonding and proton transfer, and is also the inventor on ten patents in the field of fuel cell membranes.

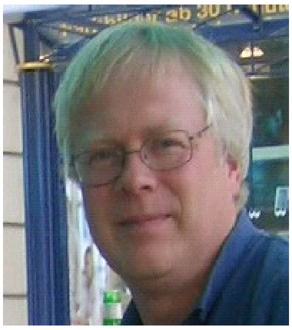
## Dr. Juhan Subbi

**SeniorResearch Scientist**
**National Institute of Chemical Physics and Biophysics, Tallinn**

Dr.Juhan Subbi graduated from Tartu University 1976 in physics, and obtained Ph.D. degree there in 1985. Has worked in optical spectroscopy of molecules and in mass spectrometry of gas discharge plasmas and biomolecules. From 2001 is actively involved in SOFC materials research and sofc development in collaboration with Elcogen AS.

## Prof. John TS Irvine

**Professor, University of St Andrews**



John Irvine is Professor of Chemistry at the University of St Andrews and currently holds an EPSRC Senior Fellowship. His first degree is in Chemical Physics from Edinburgh University and he obtained a DPhil from the University of Ulster in Photoelectrochemistry. He performed his postdoctoral studies working with Anthony West in Aberdeen and was subsequently appointed to a BP/RSC fellowship, lectureship and senior lectureship at Aberdeen University. In 1994 he was visiting Professor at Northwestern University and then moved to the University of St Andrews as Reader and then Professor of Inorganic Chemistry. His research interests are in solid state ionics, new materials, ceramic processing, electrochemistry, fuel cell technology, hydrogen, photoelectrochemistry, electrochemical conversion and heterogeneous catalysis.

## Dr. Christian Jordy

**Senior Research Scientist**
**SAFT, Direction de la recherche, Bordeaux, France**

Present Position at Saft Batteries: Senior Scientist in charge of developing new high capacity materials for positive and negative electrodes.He earned his engineer degree in chemical engineering (ENSIC, Nancy) in 1989 and his PhD in 1993 in metallurgy on new Ni-MH battery material (University Pierre et Marie Curie, Paris 6). Working at Saft since 1993, first on NiMH batteries in research (4 years) and in development (4 years). Then, he was in charge of developing positive materials for Li-Ion batteries for 4 years. Since 2007, he is in charge of prospective Li-Ion systems. Confirmed experience on new anode and cathode material design, electrode formulation, cell design, safety, ageing mechanisms of Ni-MH and Li-Ion batteries.

## Mr. Ari Auvinen

**Senior Research Scientist**
**VTT Technical Research Centre of Finland**

MSc Tech Ari Auvinen is leader of VTT Fine particles team. He has over 10 year experience in aerosol science including nuclear safety, production of aerosol based nanomaterials and emissions from combustion processes. He has 17 peer-reviewed journal publications, four patents in the field of nanoparticle synthesis and more than 100 other publications.

## Pritesh Hiralal

**Research Scientist**
**Nokia Research Centre, Cambridge**

Pritesh Hiralal is a researcher at the Nokia Research Centre in Cambridge, were he studies nanomaterials for novel form factor energy storage devices. He completed a Phd at the Electrical Engineering Department at the University of Cambridge studying 1-D nanomaterials for energy generation and storage. His main research interests are the fields of photovoltaics, batteries and supercapacitors, as well as in material growth, where he holds a number of publications and patents.

## Dr. Mario Conte

**Senior Researcher**
**ENEA – Italain National Agency for New Technology, Energy and Sustainable Economic Development**

Dr. Conte is the responsible for ENEA's Energy Storage Systems Co-ordination Unit. At ENEA, he has been carrying out research activities on batteries, supercapacitors, hydrogen storage and their applications. He graduated in nuclear physics at Naples University and started working at ENEA on energy storage systems in 1984. He is involved in numerous EU projects on advanced supercapacitors and on batteries and their applications in electric and hybrid vehicles. He has been lecturer in University courses on specific topics of energy storage systems and electrically-driven vehicles. He is author of numerous peer-reviewed publications, book chapters and encyclopaedia chapter.

## Dr. Thomas Malkow

**Scientific Officer, European Commission, Directorate-General Joint Research Centre, Institute for Energy, Petten**

Thomas Malkow studied Material Science at the Martin-Luther Universität Halle-Wittenberg and received his PhD on long term behaviour of high temperature fuel cell metallic interconnector materials from the RWTH Aachen in 1998 while conducting research at the Forschungzentrum Jülich. He did postdoctoral work at Newcastle University on mechanical properties of carbon nitride thin films and at the Institute of Advanced Materials of the Joint Research Centre Petten (JRC) on corrosion behaviour of steels in incineration environments. He then took up a scientist position at the Institute for Materials Research III of the Forschungszentrum Karlsruhe (now KIT) to investigate the corrosion behaviour of martensitic steels in lead-bismuth for accelerator driven systems.

## Prof. A.K. Shukla

**Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore**

Prior to this, on lien from Indian Institute of Science during 2003–2009, Professor Shukla provided leadership to Central Electrochemical Research Institute (CECRI) at Karaikudi as its Director, and helped transform CECRI into a leading centre in Fuel Cell R & D and Engineering. Professor Shukla has made extensive science and engineering contributions to the field of renewable energy, materials chemistry and electrochemical science and technology through interdisciplinary research during the last 30 years, in particular, for investigations leading to novel electrocatalysts, superior lithium-ion cathodes / anodes, polymer electrolyte membranes, mixed-reactant fuel cells and low-cost high energy-density lead-acid batteries with special mention to self-supported polymer electrolyte and direct borohydride fuel cell systems.

## Dr. Carsten Cremers

**Team Leader Fuel Cells**
**Fraunhofer Institute for Chemical Technoloy ICT**

Dr. Cremers was born in 1970 in Krefeld, Germany. He studied Chemistry at the University of Düsseldorf, from where he received his PhD in 1998. He is working in the field of fuel cells since 2000 when he assumed a position as project leader for a reformer project at the Technische Universität München. He became Team leader at the TUM and later at the ZAE Bayern working on Direct Methanol Fuel Cells. In 2006 he joined Fraunhofer ICT where he beacme teamlaeder in 2010. His work concerns direct alcohol fuel cells with focus on electro-catalysts for direct ethanol and direct ethylene-glycl fuel cells based on anion exchange membranen technology.

## Dr. A.M. Kannan

**Fuel Cell Research Lab, Engineering Technology Department**
**Arizona State University**

Arunachala Nadar Kannan earned his Ph.D. degree in 1990 from the Indian Institute of Science, Bangalore with a focus on Metal/Air Batteries and Alkaline Fuel Cells. Kannan has been involved in Fuel Cell and Battery research and development for the past 25 years. Since 2005, he is an Associate Professor at the Engineering Technology Department, Arizona State University. His area of expertise and research interests include low temperature Fuel Cells including Bio-Fuel Cells, more specifically nano-scale electrocatalysts and electrode active materials, Carbon Nano-tubes, Gas diffusion layers, structure-property relationships through physicochemical characterization and fabrication, Simulation/ Modeling, evaluation of single cells and multi-cell Proton Exchange Membrane Fuel Cell stacks.

## Dr. Sanna Carlsson

**Research Scientist**
**VTT Technical Research Centre of Finland**

Dr. Sanna Carlsson graduated as M.Sc.(Tech) from Helsinki University of Technology in 2002 and as D.Sc.(Tech.) from the same university in 2009. Her doctoral studies concentrated on the utilization of electrochemical methods for solving biological and pharmaceutical problems. Dr. Carlsson's research career continues at VTT, where she started as a postdoctoral scientist in 2010. Her research interests at VTT include novel flat and printable enzymatic batteries and a battery concept based on conducting polymer coated cellulose. Dr. Carlsson has also worked a short period at the administration office of the Academy of Finland.

## Dr. Jyotsna Dutta Majumdar

**Associate Professor**
**Indian Institute of Technology Kharagpur**

Dr. Dutta Majumdar is serving for the Department of Metallurgical and Materials Engineering, Indian Institute of Technology Kharagpur as an Associate Professor. Her areas of specialization include laser materials processing, surface engineering, biomaterials and nano-structured materials. The main research activity concerns application of coatings (for dstructural and functional applications), it's characterization and property evaluation to conclude on the process optimization by a detailed structure-property process parameters correlation. She has supervised 14 nos. of M. Tech (Masters of Technology) projects, one M. S. project and 4 nos. of Ph. D till date. She has published 76 papers in international journal of repute, 3 book chapters and 34 papers in the Conference Proceedings till date.

## Vijayamohanan K Pillai

**Acting Director, CSIR-CECRI**
**Scientist, CSIR-NCL, Pune, INDIA**

Vijayamohanan K Pillai received his Ph.D. from the Indian Institute of Science, Bangalore before joining the faculty of the National Chemical Laboratory, Pune. He has authored over 200 publications and 20 patents. His research interests include Materials Electrochemistry, functionalization of carbon nanotubes and hybrid materials for fuel cells, supercapacitors and rechargeable batteries. He has received several awards and fellowships like MRSI Medal, Materials Research Society of India, Bangalore, 1996, Chemical Research Society of India,(CRSI) Bronze Medal, in 2004, Member, Editorial board of Bulletin of Materials Science, 2005 onwards, and Fellow, Indian Academy of Sciences, Bangalore, 2008. He may be contact at vk.pillai@ncl.res.in

## Dr. Rossella Giorgi

**Research Scientist**
**ENEA Materials Technology Unit, Rome Italy**

Rossella Giorgi is responsible of the Surface Technology Laboratory of the Materials Technology Unit at ENEA, the Italian National Agency for New Technologies, Energy and Sustainable Economic Development She received her degree in Physics, summa cum laude, from the University of Pavia in 1975. In 1980 she took a permanent researcher position at ENEA. Here she founded the Surface Analysis Laboratory, leading a research group working in the field of electron spectroscopy. Since 2000 she has leading a research group focused on carbon based nanomaterials by CVD processes and their application to the energy field. She is co-author of more than 130 scientific papers and communications to national and international conferences.

## Dr. Sugata Mukherjee

**Associate professor**
**S.N.Bose National Centre for Basic Sciences, India**

Dr. Sugata Mukherjee is a theoretical condensed matter Physicist having worked in areas of Nanomaterials, Surface Science, Ultrafast processes in Nanomaterials. He obtained his doctoral degree from Free University Berlin and worked at Ecole Polytechnique Federale, Lausanne, Free University Berlin, Fritz-Haber-Institute of Max-Planck Society and at Helsinki University of Technology, Espoo, before joining S.N. Bose national Centre for Basic Sciences in Kolkata. His current research involves in first-principles calculations of the electronic properties of carbon and boron nitride based nanomaterials. He is a co-PI of a project under EU-India EICOON project. E-mail: sugata@bose.res.in

## Prof. Esko Kauppinen

**Professor of Physics at Aalto University**

Professor Esko I. Kauppinen is a full tenure track Professor of Physics at Aalto University. He has held the Nanotechnology Research Professor Position at VTT, Technical Research Center of Finland 2000–2010. Novel Carbon NanoBud (CNB) material was invented in his research. He has published more than 620 scientific papers and presentations, including more than 180 fully reviewed original journal articles e.g. in Nature Nanotechnol., Nano Letters, Angew. Chem., PRL and JACS and holds 17 patents. He has given more than 60 invited international conference talks and more than 140 invited talks at companies and at world leading universities, including Nokia, Samsung, NEC, NTT, Fujitsu, Toyota, HP, MIT, Tokyo University, Kyoto University and the University of Cambridge.

## Dr. Kai Savolainen

**Research Professor, Nanosafety Research Centre**
**Finnish Institute of Occupational Health**

Kai Savolainen, MD, PhD, is currently Research Professor and Director of Nanosafety Research Centre at the Finnish Institute of Occupational Health. His research interests cover toxicology and safety assessment of engineered nanoparticles in the occupational and general environment. He has especially conducted research on immunotoxicology of engineered nanomaterials and exposure to these materials as well. Kai Savolainen has coordinated several large EU projects and currently organizes a large NANODEVICE project with 26 partners.

## Dr. Rüdiger Kötz

**Group Manager**
**Paul Scherrer Institut, Switzerland**

Dr. Kötz received his Ph.D. in Physics from the Technical University Berlin in 1979. After postdoctoral years at the Case Western Reserve University in Cleveland, Ohio and at the Fritz Haber Institut der Max Planck Gesellschaft in Berlin, Dr. Kötz joined the ABB Corporate Research Centre in Baden, Switzerland in 1982. Since 1989 he has been leading the capacitor and interface analysis group of the Electrochemistry Laboratory at Paul Scherrer Insitut (PSI) in Switzerland. Throughout his career his research continued to aim at the characterization of the solid electrolyte interphase, the understanding of electro-active materials and the extrapolation of electrochemical processes to application.

## Prof. B.R. Mehta

**Professor. IIT Delhi, New Delhi, India**

Prof (Dr) Bodh Raj Mehta is currently Professor of Physics at Indian Institute of Technology Delhi, New Delhi, India. He did his M Sc in Physics from Punjabi University Patiala, M Tech in Solid State Materials and Ph D in Physics from IIT Delhi. He has worked as post-doctoral fellow at University of British Columbia, Canada; guest scientist at University of Saarbrucken, Germany; and guest professor at University of Duisburg, Germany. He has special interest in developing and teaching nanotechnology curriculum and his research interests include Nanoparticle-hydrogen interaction in Rare earth metals and Pd-alloy nanoparticles; organic-inorganic interfaces for resistive memory, light emitting and solar cell devices.

## Dr. Jorma Jokiniemi

**Professor**
**VTT Technical Research Centre of Finland and**
**University of Eastern Finland**

Key persons in the project will be: Professor Jorma Jokiniemi, Research Professor at VTT and Professor at University of Eastern Finland, PhD 1990, work history Univ. of Helsinki, VTT, EPRI (USA), Univ. of Kuopio, VTT over 25 years experience on nanoparticle and aerosol research. Supervised 9 doctoral thesis. (97 peer-refereed and more than 500 other publications.)

## Dr. Sourav Pal

**Director**
**National Chemical Laboratory, Pune**

Dr. Sourav Pal is a Director of National Chemical Laboratory. Dr.Pal is a distinguished theoretical chemist. He has contributed to diverse areas of theoretical chemistry which span the intellectually demanding and challenging aspects of methodological and conceptual developments. His contribution to the response theory formulation for closed and open shell atomic and molecular systems is well recognised in India and abroad. He has contributed significantly to the area of chemical reactivity and density functional theory response. In recent years has contributed to the catalytic and hydrogen storage materials using computational material science to interesting chemical applications.

# ABSTRACTS OF THE ORAL PRESENTATIONS

# On the EU SET-Plan and EERA with perspectives on nanomaterials for electrochemical energy converters

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The EU Strategic Energy Technologies plan (SET-plan) sets out an ambitious agenda in research, innovation and demonstration, to be lifted by public research organisations (PROs) and industry, in order to deliver on the climate change mitigation targets of the EU. For the 2050 time frame these imply very deep reductions in $CO_2$ emissions associated with production of electricity, transport and other energy related services. To minimise costs to society and reap opportunities in terms of job creation the SET-plan foresees radical evolution of existing technologies and emergence of new technologies for the 2050 time frame. The European Energy Research Alliance (EERA) seeks to maximise the efficiency and effectiveness of European energy research effort by coordination research efforts, establishing a common strategy, work plan and division of tasks among the participating PROs.

With an increased share of renewable energy resources in the energy mix the system needs to be accommodating of fluctuations in production in addition to fluctuations in consumption. Energy storage and conversion will be essential, with deployment in many parts of the energy system and serving an array of purposes including peak shaving, trough filling and ancillary services such as spinning reserve. Storage can be in the form of batteries or via conversion of electricity to synthetic fuels which are storable and also benefit from own distribution networks, depending on fuel type. In the transport sector electrical storage and synthetic fuels are likely to be essential to reducing emissions. EERA has thus focus on energy storage and conversion systems in launched Joint Programmes and in planned programmes.

# Thin Film and Nanomaterial based solar cell technologies

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Thin Film technology offers flexibility in device design and fabrication by providing a variety of options for substrates, materials and deposition methods. Such versatility allows engineering the material properties and device structure suitable for large area high volume manufacturing of these devices. However in reality, thin-film device fabrication is highly complex process that requires proper control of the layer properties over the entire process sequence. Appropriate understanding of strength and weakness of deposition techniques and the sensitivity of layers to the sequential deposition steps typically used in manufacturing are highly critical in successful commercialization of this technology. Research and development in new, exotic and simple materials and devices, and innovative but simple manufacturing processes need to be pursued in a focused manner. The status of thin film and nanomaterial research with a focus on application for solar cell devices will be reviewed in this presentation. Which solar cell (s) and which technologies will ultimately succeed commercially continue to be anybody's guess but it would surely be determined by the simplicity of manufacturability and the cost per reliable watt. Cheap and moderately efficient thin film and nanostructured solar cells are expected to receive a due commercial place under the sun.

# Nanoscience and nanotechnology in low temperature fuel cell research

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Fuel cells have been discussed intensely in the last decade as efficient energy converter for various applications, including mobile, stationary and portable applications. Fuel cell technology, which includes not only the fuel cell itself, but also the generation, processing and storage of suitable fuels, relies heavily on catalytic, electrocatalytic and, because of its potential for $H_2$ production, photocatalytic processes. In all of these processes, nanoscience and nanotechnology may play an important role not only in the technical improvement, but also for the fundamental understanding of the ongoing processes.

Concentrating on the actual electrocatalytic processes, I will discuss the role of nanoscience and nanotechnology in basic research on this topic, using simple electrocatalytic reactions and processes as example. First, the catalytic function of highly active bimetallic catalysts in fuel cell relevant reactions such as H adsorption/oxidation, CO oxidation and O2 reduction will be elucidated on a molecular scale using structurally well defined planar bimetallic model catalysts and model electrodes, where the structural properties are determined by atomic resolution scanning tunneling microscopy. This way, the chemical properties of individual adsorption ensembles become experimentally accessible and can be compared with theoretical results.

Second, the role of transport processes in fuel cell reactions will be examined, employing nanostructured electrodes with well defined arrays of ultramicroelectrodes (UMEs). Finally, the potential of such model studies, in combination with theory, for the molecular scale understanding of fuel cell relevant reactions and later applications will be discussed.

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# Materials and design challenges in solid oxide fuel cell

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Fuel cells are electrochemical devices that can convert chemical energy of a gaseous fuel directly into electrical energy. It is a conversion device that can theoretically produce electrical energy as long as the fuel and oxidants are supplied to the system. Since its efficiency is not limited by the Carnot cycle, it has the potential of operating at a much higher efficiency (> 50%) than that possible with similar energy conversion devices. When hydrogen is used as fuel, the cell produces only water as the reaction product. Hence, it is considered as one of the most environmentally benign power generation technology. As the name implies, solid oxide fuel cell (SOFC) comprises porous electrodes (anode and cathode) and a dense ceramic (solid oxide) electrolyte and operates at high temperatures (500–1 000°C). The high operating temperature allows internal reforming, promotes rapid electrocatalysis, and produces heat as one of the byproducts for cogeneration and boosting the overall efficiency. Since output from a single cell is only ~ 1V, an actual SOFC is a stack of several cells arranged in planar or tubular geometry connected in series through inter-connect.

The SOFC operating temperature, design and choice of electrolyte/electrodes are closely inter-related. The focus of SOFC development over the years has shifted from high temperature (HT-SOFC, 900°C) to intermediate temperature (IT-SOFC, 700–900°C) and recently to low temperature (LT-SOFC, 500–700°C). With lowering of operation temperature, however, a number of problems arise that are associated with materials and process kinetics (e.g., increase in electrolyte resistance/impedance and electrode polarizations). These factors have a detrimental effect on the overall electrochemical performance of the cell. Design and development of new combinations of electrolyte and electrode materials that reduce such losses are therefore a critical challenge for advancement of SOFC technology.

The present talk will discuss some of the recent developments related to SOFC technology pursued at CSIR-CGCRI and IIT-Kharagpur and highlight the major technological challenges to be overcome for successful commercialization.

# Nanomaterials in commercial PEM and DMFC fuel cell applications

Steen Yde-Andersen

CEO, IRD Fuel Cells LLC, Denmark

The step from small-scale prototype manufacturing to real products for making fuel cells a commercial success is a major challenge. Superior materials performance and their and impact of the various operating conditions, study of components integrity is mandatory to tailor the right approach leading to further performance enhancement, reduced cost and enhanced durability.

The presentation will include discussion of the state-of-the art nanomaterials, their performance and latest results from the development aimed for commercial fuel cell applications.

# Some advances in nanomaterials for PEMFC

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Aggregates, Interfaces and Materials for Energy, ICGM,
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Nanomaterials are endowed with particular properties compared to their bulk counterparts by confining their dimensions and because of the effect of surface properties on their behaviour. They have enormous potential for further development in applications in energy storage or energy conversion devices, such polymer electrolyte fuel cells where, as electrocatalysts and electrode supports and in ionomer membranes, they form the membrane electrode assembly. Platinum group metal catalysts are the larger contributor to the cost of the fuel cell stack. To reduce the costs, the platinum loading must be further decreased, without loss of catalyst performance or curtailment of lifetime: by tailoring the Pt nanoparticle size, by alloying platinum, and by using other materials to entirely replace platinum. Nanostructured carbon nanotubes and nanofibres are catalyst supports for PEM fuel cells. Non-carbonaceous materials with controlled dimensionality and composition are under study as alternatives, with enhanced corrosion resistance during operation. Much effort has been made to improve perfluorosulfonic acid ionomers and develop alternative polyaromatic and polyheterocyclic polymers and nanostructured membranes of controlled morphology. Modified membranes containing nanocrystalline inorganic fillers have been demonstrated to operate up to 150 °C. Nano-engineered block copolymers provide a protogenic-group carrying functionalised segments of controlled length and segments providing mechanical strength and phase separation. Single nanofibres of electrospun PFSA display conductivity an order of magnitude higher than the bulk, due to orientation effects, while polymer electrospinning can provide a highly porous membrane reinforcement, limiting membrane swelling in water. This presentation will shortly review recent advances in functional nanostructured materials for PEMFC.

# Nanomaterials in SOFC manufacturing – Benefits and disadvantages

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Nanostructured materials provide list of new properties compared to their "normal" micron-range counterparts due to dominant role of surface or grain interface areas compared to the bulk. This can make materials more active chemically, enhance catalytic activity, make powders more easily sinterable, and change ionic or electronic conductivity through dominant role of grain boundary region. These changes are related to a considerable amount of free energy in the surface or crystal interface regions, making nanomaterials thermally less stable, and prone to structure changes (coarsening) in catalysis. In many ways, they can be viewed as metastable materials.

For SOFC, this opens additional possibilities for matching materials properties for production, and achieving higher catalytic activities in electrodes. However, as SOFC are working at temperatures from 600 to 800 C for thousands of hours, there is a tradeoff between activity of the electrodes achieved through increasing the active area and long term stability of the structure.

For production it is best, if we can use cheap, high volume methods: tape casting and screen printing with cofiring. For that we need matched sintering temperatures and shrinkages of different layers made of different materials. In addition, we need porous electrode layers and dense electrolyte layers in the same structure, and here all the flexibility offered by combining different nano- and microstructured materials is very welcome.

In the final product we have a "conflict of interests". We need high catalytic activity in both anode and cathode that is facilitated by high surface area provided by nanostructure. On the other hand, low gas diffusion resistance is facilitated by bigger pores and coarser structure. In addition, long term stability of the element is better for a coarser structure. So here are important tradeoffs included that can be adequately addressed only through long and painstaking experimental work.

# Nanostructural engineering of SOFC electrodes

John T.S. Irvine

School of Chemistry, University of St Andrews, UK

The impregnation of electrode precursor solutions is a very powerful technique for creating novel electrode microstructures constrained within preformed scaffolds. Here we report on the microstructural evolution of Mn-containing perovskites impregnated into yttria stabilised zirconia scaffolds on heating and redox cycling. Good performances have previously been reported for SOFC anodes with similar structure and our objective is to better understand the origins of this good performance. For $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ a remarkable thin coating with microfissures is formed on the scaffold after firing the electrode precursors at 1 200°C, such behaviour can be considered as wetting of one oxide by another. On further treating this microstructure at 800°C in $H_2$ the microstructure changes dramatically forming an interconnected array of ~10nm scale particles. This seems to offer a very attractive structure with extensive triple phase boundary regions where electrochemical reactions can occur. On re-oxidation at this temperature the particles reagglomerate to form a structure approaching the initial smooth coating. This favourable interaction between the Mn containing perovskites and the zirconia scaffold is associated with a chemical interaction between impregnated oxide and substrate. The strength of this interaction decreases on reduction allowing the perovskite electrode to form nanoscale.

# Advantages and drawbacks of nanomaterials for battery applications

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Interest for nanomaterials has recently strongly risen for many applications (like electronics, chemistry, biology, energy) due to the possibility to miniaturize and also thanks to their specific physical and chemical properties like for example optical, mechanical and high chemical reactivity. Electrochemistry is not an exception to the applicability of nanomaterials; their main properties used for batteries are:

- their high specific surface area which increases chemical reactivity
- their low particle size which enables:
    - to decrease the diffusion path in active material improving the high rate performance
    - to minimize the amount of inactive material like the conductive network which is required for low conductivity active materials
- their small size makes unlikely fragmentation of active material.

Another interesting property of nanoscale materials is their ability to withstand large volume variations. This characteristic is very useful to design new high capacity silicon anode for lithium-ion batteries. Compared to micrometric particle size, the nanosized silicon shows longer cycle life since the particle size should be stable during successive 300% swelling and contractions occurring during charge and discharge; moreover the nano displacements cause less strains of the conductive network.

Nevertheless, the use of nanomaterials has also some drawbacks in electrochemistry. For example, when they are used in negative electrode for lithium-ion batteries it increases the irreversible capacity. This is due to side reactions occurring between electrolyte and active material combined with the high specific surface area of nanosized materials. For the same reason, the positive electrode materials for Li-Ion batteries generally show lower thermal stability properties at charged state when very fine particles are utilized.

Therefore, nanomaterials should not be systematically chosen for the design of new materials for battery application since a trade-off has generally to be made between the improved kinetics, cycle life and thermal stability.

# Synthesis of SiO nanoparticles for Li-ion batteries

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Induction nucleation is a very well suited technique for large scale synthesis of various nanomaterials (Auvinen et. al, 2010) Using induction materials can efficiently be heated to a very high temperature thus enabling high production rates. At the same time the gas flow can be kept cool, which induces extremely high temperature gradients needed for formation of nanoparticles. The synthesis can be carried out at normal pressure, which significantly decreases the facility costs as well as the pumping power. At the outlet of the furnace also the temperature of the inert gas flow is close to ambient enabling the use of common structural materials, rubber seals and inexpensive bag filters. Typically the precursors can be relatively low-cost and yet high purity bulk materials. Induction nucleation process is also environmentally sound as it uses no water, produces no liquid waste and releases only filtered nitrogen from the reactor.

The induction nucleation method was initially developed for production of metallic nanoparticles. The source materials are vaporised from tungsten or graphite crucibles to nitrogen or argon carrier gas flow. Graphite felt insulation separates the hot carrier gas from cool nitrogen flow. When the gas flows are mixed turbulently, rapid cooling induces formation of nanoparticles.

In this work the same method was applied for production of SiO nanoparticles applied in Li-ion battery anodes. SiO is well suited for material for induction nucleation synthesis as it has significantly higher vapour pressure than either Si or SiO2. It is also far less reactive in high temperatures than pure silicon. SiO particles were produced by heating silicon in contact with oxides in temperature varying between 1 600°C to 1 790°C. The highest mass concentration reached in the tests was 2 600mg/m$^3$ at 1 790°C. The produced particles were amorphous with primary diameter of about 15 nm. In the gas phase the primary particles formed larger agglomerates with mobility diameter of about 150 nm.

Also production of SiO-Cu composite particles was tested by placing the source materials either in the same or in separate crucibles. With single crucible set-up the copper content of the produced powder ranged from 2 wt-% to 4 wt-% depending on the test parameters. A two-crucible set-up allowed more freedom in tuning the copper content of the particles.

This study belongs to Active Nanocomposite Materials project funded by Tekes under Functional Materials Program.

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# Nanomaterials for Supercapacitors: Enhancement and novel properties

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Carbon based high surface area electrodes are desirable for stable higher density energy supercapacitors. A large number of novel forms of nanocarbon are available which provide high promise for properties such as higher energy densities, higher power densities, flexibility, and even transparency. However, the ultimate performance achieved depends not only on the material itself, but on the particular architecture used for the electrode. This work describes supercapacitors made with various forms of high surface area carbons, activated carbon, carbon nanotubes(CNTs) and carbon nanohorns (CNH) and shows the effect and the different benefits which may be achieved with different electrode architectures.

Multiple properties of CNTs make them ideal as electrode materials for supercapacitors; namely their large surface area, their high electrical conductivity and their chemical stability. However, thus far their use in supercapacitors has been limited to laboratory devices due to several factors including material cost and quality, deposition methods and performance. For CNT based electrodes, the growth method, the deposition method, the type/quality/purity of material and the resulting physical arrangement have a large effect in performance. Here we report on the fabrication of two-electrode electric double-layer capacitor (EDLC) cells, and study their performance as a function of several types of CNTs architectured in multiple ways. We compare the merits of each architecture and propose a recipe for an ideal CNT based supercapacitor.

Electrodes consisting of flat, random, conducting networks of SWNTs or MWNTs can be produced by vacuum filtration. This low temperature process can be used to deposit CNTs on a large variety of substrates, and films can be made transparent and conducting by controlling the thickness. These electrodes provide multiple possibilities including mechanical flexibility and transparent devices.

Alternatively, forests of MWNTs, ~10s of μms in length can be grown onto Si substrates and transferred via a simple rolling mechanism onto the desired electrode or used as self standing films. These result in dense, aligned films with high conductivity, thus removing the requirement for a metallic current collector and maintaining flexibility without the use of a binder. Finally, oriented CNT forests can be grown directly onto the desired charge collector foil. Although the resulting quality of the tubes is somewhat lower due to the temperature constraints of foil growth, the resulting electrode is an excellent template and can be optimized to have a low contact resistance with the charge collector.

Overall, CNTs are shown to be a suitable candidate for constructing supercapacitors, however strategic optimization is needed to optimize the architecture in order to exploit the full potential of the material. CNT arrangement has a large effect on capacitance (ranging from ~5 to 35 F/g), on equivalent series resistance (20–160 Ω) and on the resulting power densities. CNHs may be combined with the CNTs in a hierarchical fashion in order to enhance both power and energy density. A novel hybrid nanocarbon structure is demonstrated which combines the advantages of both forms of carbon.

Finally, some of the novel properties which may be achieved with these architectures are demonstrated such as flexibility tolerance and transparency, enabling electrochemical storage devices with novel form factors.

# Supercapacitors: materials, performances and applications

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The need to improve efficiency and sustainability of energy systems in all the aspects from generation up to the end uses is motivating the research and development of new storage systems and methods. The variety of existing or projected applications ranging from consumer electronics, electric and hybrid vehicles up to large power generation plants and electricity distribution grids with improved power quality and larger introduction of renewable energy sources requires storage systems with extremely varying performance characteristics.

There are many alternative methods available to meet all technical and economical requirements from a growing spectrum of applications. Electrochemical batteries, SMES (superconducting magnetic energy storage), pumped hydro, flywheels, CAES (compressed air energy storage) and hydrogen storage are all possible solutions for storing energy usually proposed with no ideal choice among them. The supercapacitors (SCs), also called ultracapacitors or electrochemical capacitors, are devices with a very high specific power and high capacitance, available for a long period of time with negligible deterioration, that have been historically proposed in small applications (memory back-up in consumer electronics, storage systems for micro solar power generators) and now are proposed for high power/energy applications, such as hybrid and electric vehicles, power quality systems and smart grids. The advancements in new materials and the rapid growth of more demanding storage systems in a variety of applications have created a need of better comprehension of these devices in terms of designs and performances characteristics.

This presentation is mainly aimed at a brief survey of the history of the SC development, which is strongly related to the evolution of the SC technologies and their constituent materials. The description of the various categories of SC will be presented according to a defined classification in symmetric, asymmetric and hybrid and the most used materials. The basic characteristics of the SC will be described in relation to the measuring methodology. Finally, the high energy and high power new applications of large SC devices will be shortly described, with focus on transport, industrial and electric utility sectors.

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# Nanostructured Materials for Electrochemical Energy Systems

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This lecture will describe our efforts on the development of electrodes and electrolytes for use in electrochemical energy systems. We have been working on catalysts for small molecule oxidation to be used in direct fuel cells as well as development of electrode materials for capacitors. The second aspect of our research is related to the studies on the use of molten electrolytes for rechargeable magnesium and zinc batteries.

**Sampath and co-workers**

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# Assessment of mutual EU-India Nanomaterials research needs and researchers training needs in the field of sustainable energy technologies: The outcome of the previous EICOON workshop

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The EICOON (Euro-Indo forum for Nanomaterials research coordination & cooperation of researchers in sustainable energy technologies) project funded in part by the European Commission under the 7th Framework Programme on Research, Technological Development and Demonstration of the European Union (EU) is about the assessment of the Nanomaterials research needs and researchers training needs in the field of sustainable energy technologies in regard to the EU and India to eventually draw up a list of research topics of mutual interest to both regions for a future coordinated call for research proposals. In this frame of the project, a workshop and School on Nanomaterials for Sustainable Energy was held in early November 2010 in New Delhi, India to gather supplementary information on the said needs especially from stakeholders and to educate researchers active in the field as well as interested students on the topics of Nanomaterials for selected sustainable energy technologies. The results of these events are summarized including a list of suggested topics for a future coordinated call as have been identified being of mutual EU-India interest.

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# Hybrid ultracapacitors and their applications

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Hybrid ultracapacitors and their applications A K Shukla Solid State & Structural Chemistry Unit Indian Institute of Science, Banaglore Capacitors store electrical charge. Generally, the charge is stored physically as equal quantities of positive and negative charge separated on opposite faces of an insulating material. When the two faces are connected by an external current path, current flows until complete charge balance is achieved. The capacitor can then be returned to its charged state by applying voltage. Because the charge is stored physically, with no chemical or phase changes taking place, the process is highly reversible and the discharge-charge cycle can be repeated over and over again without limit. In recent years, electrochemical capacitors that are also referred to as ultracapacitors have emerged as promising storage devices. Ultracapacitors can be divided into three general classes: electrical double-layer capacitors, pseudo-capacitors and hybrid capacitors. Each class is characterized by its unique mechanism for storing charge. These are, respectively, non-faradaic, faradaic and a combination of the two. Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between electrode and electrolyte. A non-faradaic mechanism, by contrast, does not use a chemical mechanism, and rather, charges are distributed on surfaces by physical processes that do not involve the making or breaking of chemical bonds. Some of the recent R&D work on hybrid ultracapacitors and their applications will be highlighted.

# Direct alcohol fuel cell development based on different low temperature fuel cell technologies

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Due to the high energy density of the liquid fuels and their easy handling direct alcohol fuel cells have a large potential e.g. as portable power sources for consumer applications or as smaller scale back-up power solutions. However, the potential customers are often still not accepting methanol as fuel, mainly due to its toxicity. Furthermore, the achievable power density and the costs for the used platinum based catalyst limit the use of today's DEMFC to systems with not more than about 1 kW power and to high-value applications. The market share of DAFC could be enlarged if less expensive cells operating on other fuels than methanol can be established. Allowing for the use in portable and back-up power solutions, low temperature systems are preferred.

A promising alternative are alkaline anion exchange membrane fuel cells (AEMFC) with their potential to use base metal or non-platinum based catalysts. Detailed studies on the oxidation of ethanol and ethylene glycol under alkaline conditions have been performed [1–5]. In stripping experiments it could be shown, that the adsorption of the $C_2$ alcohols onto a clean polycrystalline platinum surface proceeds via breaking of the C-C bond. In presence of bulk fuel the surface gets however poisoned by part of these adsorbates [6]. In consequence, $C_2$ products are formed most likely because of the unavailability of two adjacent surface sites for C-C bond splitting. This seems to be similar for the situation in acidic DEFC where the $CO_2$ current efficiency was shown to depend on the number of surface sites [7]. An important difference is the kind of $C_2$ product which is mainly acetate in the alkaline and mainly acetaldehyde in the acidic environment. The poisoning effect of ethylene glycol is less severe as here the two C atoms are identical and lead to the formation of the same $CO_{ads}$ species. Therefore, the liberation of adjacent surface sites is more likely and $CO_2$ current efficiencies are higher as has been shown in single cell tests. An alternative approach can be the use of higher temperatures, e.g. by using a HT-PEMFC, or HT-AEMFC which are currently developed. As it will be shown, raising the temperature indeed improves the kinetics of the ethanol oxidation in acidic environment; however, it shows some unpredicted effects in alkaline solution which will be discussed.

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# Nanocatalysts for PEMFCs

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Renewable energy technologies are highly relevant for the current fuel crisis scenario faced by the entire world. Among various fuel cell types, proton exchange membrane fuel cells (PEMFCs) attract the foremost attention for automotive applications, small scale power generation for stationary/residential and portable power applications due to their lower operating temperature. However, the economical factors of the PEMFC components are the primary limitations for their early commercialization. Improving the utilization of Pt catalysts and development of high power membrane electrodes assemblies (MEAs) are the focus areas in many R&D laboratories through more accessible nanosize catalyst sites on durable catalyst support materials like CNTs and thinner active catalyst layers.

Nanosized catalyst particles show unique properties such as high specific surface area, superior catalytic activity yielding higher performance with lower catalyst loadings. Multi-walled carbon nanotubes (MWCNTs) have the significantly higher electrochemical durability (oxidative stability) as compared to carbon substrates at 80 °C. Also the Pt/MWCNTs nanoparticles has a potential to show superior chemical and electrochemical stability compared to commercial catalysts using Vulcan carbon supported Pt. However, preparing the homogeneous dispersion and controllable loading of Pt on MWCNTs is still a big challenge to the research community.

Before the deposition of Pt catalyst, MWCNTs surface was modified by citric acid to enhance its reactivity. A mild reducing agent, sodium formate was added drop-wise into the platinum precursor for obtaining Pt nanoparticles. Then the Pt/MWCNTs particles were filtered, washed, dried at 100°C before thermal treatment at 800°C for 2 hours under flowing Ar atmosphere. The catalyst coated membrane was assembled inside the single cell along with a pair of gas diffusion layers (GDLs) (fabricated by a wire rod coating with mixture PureBlack (75 wt. %) and VGCF (25 wt. %). PEMFC performance evaluations of the Pt/MWCNTs catalyst were carried out with $H_2/O_2$ at 80°C, at various back pressure and various RH conditions.

Highly homogenous dispersion of Pt nanoparticles enables excellent catalyst utilization as compared to the commercial catalyst (Pt/C). MWCNTs decorated with platinum nanoparticles in the size range 2–4 nm showed excellent FC performance and durability compared to commercial Pt/C.

# Surface species and product distribution in the electrooxidation of small organic molecules

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The electrooxidation of small organic molecules is known to proceed via more or less complex reaction networks, involving a number of stable, adsorbed or desorbed (volatile) reaction intermediates and side products in addition to the main product [1]. This is discussed for a number of C1–C3 molecules, in particular methanol and ethanol. The discussion is mainly based on own data, acquired by combined IR/DEMS measurements. These allow simultaneous in-situ IR measurements of the adsorbed species in an attenuated total reflection (ATR-IR) configuration, mass spectrometric detection of volatile reaction intermediates and reaction products by differential electrochemical mass spectrometry (DEMS) under continuous electrolyte transport, in addition to the determination of the total reaction rate reflected by the Faradaic current [2].

From numerous previous studies (see e.g., ref. [2]) it is well known that the oxidation of these molecules is rather slow, requiring significant overpotentials. More important, C-C bond breaking in C2 and C3 molecules turned out to be strongly hindered, resulting in very low $CO_2$ product yields at useable potentials, essentially regardless of the catalyst or electrode material. DEMS measurements performed at high temperatures, up to 100°C, and elevated pressure, up to 3 bar overpressure in a newly developed flow cell set-up [3], reveal a dominant role of the reaction temperature not only on the overall reaction rate, but also on the product distribution. For instance, with increasing temperature, also the $CO_2$ product yield increases rapidly, reaching, e.g., a value of ~45% for ethanol oxidation at 0.48 $V_{RHE}$ on a carbon supported Pt catalyst at 100°C [4].

The results from steady-state and transient measurements are discussed in a general reaction framework. In a more general sense, comparison will be made also between reaction in acidic and alkaline electrolyte.

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# Materials and design challenges in solid oxide fuel cell

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Fuel cells are electrochemical devices that can convert chemical energy of a gaseous fuel directly into electrical energy. It is a conversion device that can theoretically produce electrical energy as long as the fuel and oxidants are supplied to the system. Since its efficiency is not limited by the Carnot cycle, it has the potential of operating at a much higher efficiency (> 50%) than that possible with similar energy conversion devices. When hydrogen is used as fuel, the cell produces only water as the reaction product. Hence, it is considered as one of the most environmentally benign power generation technology. As the name implies, solid oxide fuel cell (SOFC) comprises porous electrodes (anode and cathode) and a dense ceramic (solid oxide) electrolyte and operates at high temperatures (500–1 000°C). The high operating temperature allows internal reforming, promotes rapid electrocatalysis, and produces heat as one of the byproducts for cogeneration and boosting the overall efficiency. Since output from a single cell is only ~ 1V, an actual SOFC is a stack of several cells arranged in planar or tubular geometry connected in series through inter-connect.

The SOFC operating temperature, design and choice of electrolyte/electrodes are closely inter-related. The focus of SOFC development over the years has shifted from high temperature (HT-SOFC, 900°C) to intermediate temperature (IT-SOFC, 700–900°C) and recently to low temperature (LT-SOFC, 500–700°C). With lowering of operation temperature, however, a number of problems arise that are associated with materials and process kinetics (e.g., increase in electrolyte resistance/impedance and electrode polarizations). These factors have a detrimental effect on the overall electrochemical performance of the cell. Design and development of new combinations of electrolyte and electrode materials that reduce such losses are therefore a critical challenge for advancement of SOFC technology.

The present talk will discuss some of the recent developments related to SOFC technology pursued at CSIR-CGCRI and IIT-Kharagpur and highlight the major technological challenges to be overcome for successful commercialization.

# Printed power sources based on renewable material

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Different kinds of disposable power source solutions will be presented in this talk. The main emphasis in the presentation is on enzymatically catalysed thin layer biobatteries or biofuel cells which have been studied at VTT in collaboration with Åbo Akademi University and Aalto University. The biobattery does not contain rare metals as catalysts and it is mainly based on renewable materials, moreover environmentally friendly final products such as gluconic acid and water are produced in the reaction.[1, 2] This kind of battery system is capable to produce enough power for RFID tags, medical plasters and other kinds of low-power applications, in which the disposability is a critical factor. Other power source types which will be discussed in the presentation include activated carbon based supercapacitors and different battery concepts based on conducting polymers. Supercapacitors are based on electrochemical double layers of two separated activated carbon coated electrodes. Supercapacitors are typically used together with other battery types to enable momentary need of large current peaks.[3] Polyaniline based battery (Pani-battery) is a combination of aluminium anode and freely breathing polyaniline cathode and can produce around 1V open cell voltage. Another polymer based battery, namely salt and paper battery concept, is based on the nanocellulosic binder for chloride doped polypyrrole electrodes and is currently under investigation in collaboration with University of Uppsala.[4] Finally, the presentation will discuss printing and other roll-to-roll methods as the mass production method for cost efficient manufacturing of the different power sources.

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# Surface modification in enhancing the efficiencies of batteries

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Batteries are facing challenges to meet the needs of consumers to improve its energy efficiency. From computers to megawatt-level grid energy storage, battery power is a crucial element for enabling today's mobile applications and large scale energy harvesting. Surface composition plays an effective role in improving the capacity retention, rate capability, and even thermal stability of cathode materials and also the anode for improving the overall efficiency of the batteries. The coating materials investigated to date include carbon, metal oxides, metal carbonates, metal aluminates, metal phosphates, metal fluorides, metal oxyfluorides, and metal hydroxides. The coating process applied for the development of a particular kind of coating also plays a role in influencing the performance. The mechanisms which are found to play positive roles are (a) electron-conducting media that facilitating the charge transfer at the surface; (b) modification of cathode surface chemistry so as to improve it's performance; (c) application of inhibitors which reduces the acidity of non-aqueous electrolyte and suppresses metal dissolution from the cathode; and (d) application of physical protection barrier that impedes the side reactions between cathode materials and non-aqueous electrolytes and (e) change in surface chemistry of anode so as to increase the overall efficiency of the batteries. In the presentation, the coating materials and techniques for the above mentioned goals would be discussed in details.

# Domain size manipulation of polymer electrolytes for improved fuel cell performance by functionalized carbon nanotubes

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The application of sulfonic acid-functionalized multiwalled (s-MWNT) carbon nanotubes to manipulate the hydrophilic domain size of Nafion membranes is explored here as an option for tuning the proton conductivity of polymer electrolyte membranes for hydrogen-oxygen fuel cells. The electrochemical impedance experiments provide preliminary evidence of increased proton conductivity, while small-angle X-ray scattering measurements line out enhanced ionic cluster domain size in these composite membranes as the central reason for higher conductivity (70A ° for the optimum composite membrane vs 50 A ° for Nafion 115) values. Scanning electrochemical microscopy indicates synergistic interaction between the sulfonic acid functional groups present in the Nafion membrane and those on the nanotube surface. More interestingly, the nanotube-tailored Nafion membranes ameliorate the performance of fuel cells as confirmed by measurements at a single-cell level, which reveal a maximum power density of 380 mW cm-higher than those of Nafion 115 (250mWcm-2) and recast Nafion (230mWcm-2) membranes. Thus, in addition to providing an elegant means of controlling the ionic cluster size, the strategic approach of using CNT both as an anchoring backbone for -SO3H groups to enrich proton conductivity and as a blending agent to improve the mechanical characteristics of the Nafion phase might be helpful in alleviating many critical problems associated with the use of commercial Nafion membranes.

# Carbon nanomaterials as support of Pt-based electrocatalysts for PMFC

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Nanomaterials can help to solve challenging problems in the field of clean energy production, conversion and storage, determining the success of the new energy devices alternative to environmentally unfriendly fossil-fuel use. The real market penetration of polymer electrolyte fuel cells is hindered by the high cost of this technology mainly due to the expensive platinum-based catalysts. The key to efficiency of PMFC is a high catalytic surface area, which can be improved by nanostructuring the catalyst and by through the appropriate choice of a high surface area support material, as the interaction between the catalyst and the support is a factor influencing the catalyst activity. Moreover a better utilisation of the catalyst is desirable, since the impregnation-reduction method used for electrocatalyst delivery in commercial electrodes does not ensure its full exploitation.

New concepts and approaches in preparing PEM electrodes have been studied by combining carbon nanostructures as catalyst support with nanostructured metal and metal alloys particles, localized only on the surface of the diffusive layer by means of unconventional deposition methods.

In this work different types of carbon nanostructures are presented as materials for electrocatalyst supports of PEM electrodes. Chemical vapor deposition processes and structural and morphological characteristics of carbon nanostructures are first discussed. Then the electrochemical performance of electrodes consisting of Pt and PtAu nanoparticles, deposited on carbon nanostructures by means of sputter deposition and electrodeposition, are compared with that of a commercial catalyst.

# First-principles study of electronic properties of two dimensional carbon and boron nitride nanomaterials

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First principles pseudopotential plane wave method was used to study ground state electronic properties of Graphene, hexagonal Boron Nitride (h-BN), Graphene doped with Boron and Nitrogen, and multilayers of Graphene and h-BN. Our results on doped Graphene indicate that upon electron (hole) doping, the Dirac-point in the electronic bandstructure shifts below (above) the Fermi level and a gap appears at the high-symmetric K-point. Upon co-doping of Graphene by both Boron and Nitrogen a small energy gap between the conduction and valence band appears at the Fermi level, making the CBN nanomaterial a narrow band semiconductor. The energy gap depends sensitively on the degree of doping and on the thickness of CBN layer. These results are in agreement with recent experimental measurements [1, 2]. Our bandstructure calculations on the multilayers of Graphene and h-BN indicate that these nanostructured multilayers exhibit semiconducting behaviour with band gap in the range 60–600 meV depending on the relative orientation and thickness of the layers. These results will be discussed in the light of available experimental data.

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# Floating catalyst synthesis and direct dry deposition of swcnts for thin film applications

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We present the synthesis of the high quality single walled carbon nanotubes (SWCNT) as well as discuss their formation mechanisms during floating catalyst CVD synthesis from CO at ambient pressure and at temperature range 800–1100°C using iron nanoparticle catalyst. We discuss the effect of reactor operating temperature on the individual tube as well as bundle length and their diameter distributions, being determined both by electron microscopic as well as optical methods (Anisimov et al., 2010; Ying et al., 2010). Especially, we discuss the control of tube chirality distributions via introducing trace amounts of $CO_2$ and $NH_3$ into the reactor.

Methods for SWCNT direct, dry deposition from the reactor at ambient temperature and pressure to manufacture transparent thin film conductors and field effect transistors (TFT) are presented. Flexible SWCNT-PET conducting films show transparency-sheet resistance properties surpassing those of ITO-PET films (Kaskela et al., 2010). SWCNT network TFTs on both silicon as well as polymeric substrates show mobilities of 35 $cm^2/Vs$ and on/off ratio of $5*10^6$. We also fabricated logic circuits on flexible substrates (Sun et al., 2011). Also, we developed free standing SWCNT films for various applications (Nasibulin et al., 2011).

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# Emerging issues on health effects of engineered nanomaterials

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The significance of engineered nanomaterials (ENM) and nanotechnologies grows rapidly. In the near future, nanotechnology-based applications will have a marked impact on human every-day life. However, very little is known of the possible risks of ENM to occupational safety and health (OSH). The exposure of workers, consumers and susceptible groups has to be though considered. However, knowledge of the exposure to, or effects of, ENM on human health and safety is limited and does not allow reliable risk assessment of ENM. Several issues related to ENM require marked attention. The most topical issues include: 1) improved understanding of ENM metrics that determine their toxicity; 2) development of monitoring devices for ENM exposure assessment; 3) understanding the changes of ENM structure and state of agglomeration at different concentrations in aerosols; 4) understanding biological effects of ENM in the human body; 5) the development of tiered approaches for testing of safety of ENM; and 6) utilizing these data for health risk assessment. Available data on several ENM – ability to enter the body and reach almost any organ, to cause pulmonary inflammation and fibrosis, and to cause increased risk of mesotheliomas in animal models, call for immediate action to identify those ENM that may cause OSH risks from those that are innocent. Thus, there is an urgent need for information that allows categorization and classification of ENM based on their biological properties. Supported by the European Union 7th Framework Program Grant CP-IP-211464-2 (NANODEVICE Project).

# Carbon nanomaterials for electrochemical capacitors

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After a short introduction to fundamental principles and applications of electrochemical double layer capacitors (EDLC) [1] – also known as supercapacitors or ultracapacitors – the presentation concentrates on carbon materials used in EDLCs for the active electrode material. These materials are typically activated carbon (AC), single walled carbon nanotubes (SWCNT) and graphite oxide (GOx) and graphene.

**Activated carbon** (AC) is the typical electrode material used in the majority of today's commercially available capacitors. AC for EDLCs have specific surface areas of 1500 m2/g or more. In order to achieve such high surface area the carbon has to be porous with pore diameters in the order of nanometers and pore wall thicknesses again in the order of nano meter. Although the performance of EDLC electrodes is mainly determined by the specific surface area [2] the pore size distribution may give rise to special effects such as the anomalous capacitance for very small pores [3]. For the investigation of such pore size affects templated carbons or carbons derived from carbides, so called carbide-derived carbons (CDC), become important. **Carbon nanotubes** (CNT), which can be grown on metal supports rapidly gained significant importance due to their specific surface properties. In particular single walled carbon nanotubes (SWCNT) provided a high specific capacitance and proved to be rather stable at cell voltages higher than the typical 2.7 V of todays capacitors based on organic electrolytes. In addition, well-aligned SWCNTs provided straight pores and good electronic conductivity resulting in low internal resistance [4]. **Graphene** and similar materials gained significant attention recently also for electrochemical energy storage applications due to their spectacular properties like high conductivity and stability. Graphene is the carbon material with the highest theoretical specific surface area of 2360 m2/g and thus particularly interesting as a high surface area electrode material [5]. Some recent results and approaches to build a good electrode from graphene sheets will be discussed.

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# Pd-H interaction in size selected Pd and Pd alloy nanoparticles

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Pd-H interaction is one of the most complex solid state-gas molecule interaction. We have utilized 'nanotechnological route' for separating the overlapping electronic, structural and topographic effects by controlling nanoparticle size and interparticle separation. An integrated deposition set up consisting of spark generator, UV radiation charger, differential mobility analyzer, in-flight sintering has been used for growing size selected Pd and Pd alloy nanoparticles. Pd-H interaction in Pd nanoparticles has been studied using an in-situ investigation of hydrogen induced changes in lattice constant, $\alpha$ to $\beta$ phase transformation as a function of H concentration and temperature. Pd-H interaction is found to be strongly related to the overlap of Pd 4d and H1s levels and density of state at the Fermi energy and gets enhanced due to size-induced shift of d band centroid. The magnitude and sign of the changes in the core and valence band levels due to size and alloying in Pd, Cu, Ag, Pd-Cu ad Pd-Ag nanoparticles has been understood in terms of lattice alteration, surface, size and charge transfer effects. Based on these results, hydrogen sensor and switchable mirror devices having unique sensor response and enhanced characteristics have been developed.

# Gas phase synthesis of anode materials for Li-ion batteries

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Both environmental concerns and advances in consumer electronics place increasing demands on efficient energy storage solutions. Currently lithium ion batteries with their high energy density and long life-time are, perhaps, the best available technology to meet these demands (Hall and Bain, 2008). However, for the widespread utilization of Li-ion batteries in applications such as electric vehicles, several challenges still remain. These include price, safety, specific energy and power, and the cycle life (Du Pasquier et al. 2003, Wen et al. 2008). For Li-ion batteries there is an interest in silicon based high specific energy materials and stable and safe materials such as lithiumtitanate for stationary applications. Gas phase synthesis of these materials is a viable option to produce these materials.

First we describes a single-stage gas phase method for the production of doped LTO. The particles were synthesised using a flame spray pyrolysis (FSP) system from a precursor solution containing Li-acetylacetonate (0.22 M) and titanium tetraisopropoxide (0.28 M). Doping with silver and copper was achieved by adding, respectively, silver and copper 2-ethyl hexanoic acid directly into the precursor solution. The resulting particles were found to be high purity, single crystalline nanoparticles with a primary particle size of about 10 nm (BET derived), and a uniform dopant distribution. The silver dopant was found to form ultrafine particles on the surface of the LTO particles. The copper, on the other hand, reacted chemically with the LTO to form what is likely a double spinel structure. Electrochemical testing of the produced material is also presented.

The other aim was to produce silicon nanoparticles at temperatures above the limit of resistance heating furnaces. High temperature required in the process is achieved with an induction heating furnace. The source metal is placed in a zirconia crucible embedded in solid graphite or other suitable conductor. The system is enclosed in graphite felt insulation. Argon flow carries silicon vapour outside the insulation, where nitrogen sheath flow rapidly cools the carrier flow and metal vapour forms nanoparticles. The temperature is monitored with a pyrometer above the furnace through a small opening in the insulations. The furnace has been tested to withstand crucible temperature at 2300°C while the temperature of the quenched gas remains below 150°C. The method to produce silicon nanoparticles with an induction heating furnace offers good repeatability in concentration and size distribution. Even with relatively large concentrations the primary particle size is small due to rapid cooling.

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# Theoretical study of binding and desorption of hydrogen on doped Magnesium hydride and light metal decorated metal-organic framework 5

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For implementation of a hydrogen economy, cost-effective, safe, and efficient storage of hydrogen is a necessary prerequisite. Storing hydrogen in solid-state materials offers the advantage of operating in a low pressure and room temperature and also improves the energy density of hydrogen in comparison to that provided by high pressure tanks and cryogenic vessels. We will discuss theoretical calculations on the effect of doping on two classes of materials, Magnesium hydrides and metal-organic-frameworks (MOF).

Magnesium hydride ($MgH_2$) is lightweight and has a low manufacture cost and a high capacity of 7.6 wt.% $H_2$. These features make it an attractive possibility for hydrogen storage. However, $MgH_2$ has a high thermodynamic stability which is responsible for the high dehydrogenation temperature requirement of 573 K. Its slow hydrogen sorption kinetics still further limits the application of $MgH_2$ for on-board hydrogen storage. Typically, it is realized that hydrogen adsorption energies should be ~20–50 Kj/ mole. In the light of the destabilization of $MgH_2$ caused by light metals and the importance of its metastable phases, study of the electronic structure, thermodynamics and hydrogen desorption kinetics of Al- and Si-doped α-, γ-, and β-$MgH_2$ will be reported using density functional calculations and the plane wave pseudopotential method.

MOFs, with their extremely high surface areas, fast $H_2$ desorption kinetics, and reversible $H_2$ uptake and release are one of the most promising class of hydrogen storage materials. However, in this case, the binding is via van der Waals interactions between the physisorbed $H_2$ molecules and the host MOFs. We discuss the results of decoration of the organic linker of MOF-5 with light metal atoms and ions to strengthen the binding.

# ABSTRACTS
# OF THE POSTERS

## Session I
## Fuel Cells

# Theoretical investigations of cathode electrocatalysts for PEMFCs

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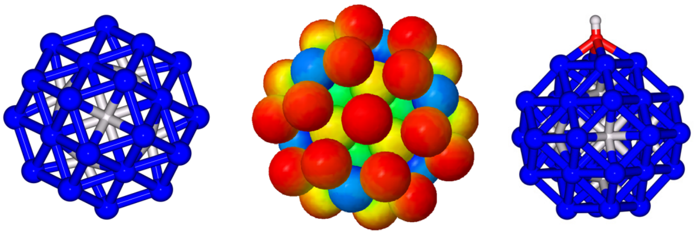
The expensive precious metal platinum catalyst is a prohibitory factor in the successful commercialisation of PEM fuel cells. Research has been focused on developing low cost electrocatalyst alternatives through theoretical investigations utilising two methods. Structural searches are performed using semi-empirical methods coupled with a genetic algorithm search routine. Density Functional Theory calculations have then been performed to accurately simulate systems, both looking at bare clusters and molecular adsorption onto the cluster surface. Focused has been placed on developing and characterising bimetallic clusters with enhancements in catalytic activity. This research has aimed to determine stable structures and compositions of bimetallic clusters for improved catalytic properties. Particular interest has been placed on core-shell nanoparticles. But cluster segregation and mixing has also been considered.

Following on from this, and taking into account other work from the group [1], adsorption of small molecules onto cluster surfaces has been studied. For example, the study of hydroxyl adsorption onto different faces of a stable truncated-octahedron structure. This allows for possible electrocatalyst design to produce more favourable Oxygen Reduction Reaction kinetics. Reaction kinetics are determined by investigating a number phenomena including bond lengths, binding energies and density of states.

Furthermore, it is possible to study adsorption of poisoning molecules in order to determine the catalysts susceptibility to them. An example of this is the study of CO adsorption which binds strongly to the pure Pt surface. Effects of poisoning molecules can be studied by looking at binding energies as well as density of states.



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# The ethanol oxidation reaction in alkaline direct alcohol fuel cells

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The electro-oxidation reaction of ethanol is a complex reaction that proceeds through multiple steps and follows a dual pathway. Several reactive intermediates and poisoning species intermediates are expected to be involved in this reaction. Some of the adsorbed intermediates are converted into the end products like acetate and carbonate and the rest being retained on the catalyst surface may cause considerable reduction of the fuel efficiency. In this work a Direct Ethanol Fuel Cell with an active area of 5 $cm^2$ was operated with different types of membrane electrode assemblies (MEA). The MEAs were equipped with commercially available anion exchange membranes as well as with self fabricated polysulfone membranes functionalised with quaternary ammonium groups.

The influence of different catalysts, anion exchange membranes and operation conditions on the product composition was investigated. The anode exhaust water was analyzed with gas chromatography and the catalysts were characterized ex-situ with a rotating disk. To characterize the state of the fuel cell in situ methods were applied. The open cell voltage and polarisation curves were recorded and diffusion current measurements were conducted.

The product analysis showed that a considerable amount of the fuel undergoes incomplete oxidation leading to the reaction products acetaldehyde and acetic acid.

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# In-situ growth of hydrophobic CNF layers on carbon microfibers and direct one-side only Pt deposition for PEM fuel cell applications

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PEM fuel cells are non-polluting and efficient energy conversion devices that are expected to play a dominant role in energy solutions of the future [1]. However, they still need to overcome technological roadblocks such as the water flooding problem and the high cost of materials, mainly platinum (Pt). To achieve higher efficiency of the electrocatalyst and reduce the usage of Pt, the catalyst has to be dispersed on an inert support with high surface area, porosity and electrical conductivity, such as carbon nanofibers (CNFs) [2].

We grow CNFs directly on a carbon paper, constituting the gas diffusion media. Firstly, metal nanoparticles are deposited on the carbon substrate. Secondly, carbon nanostructures are grown by catalytic chemical vapour decomposition. Finally, Pt nanoparticles are deposited directly on the carbon nanostructures by chemical and physical methods. Both methods ensure an even deposition of Pt nanoparticles (2–6 nm) only on the side of the electrode which is in close contact with the membrane of the fuel cell. SEM, TEM, XRF, BET, contact angle and cyclic voltammetry are used to characterize the electrodes.

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# Durability of different carbon nanomaterial supports with PtRu catalyst in a DMFC

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PtRu catalysts with similar particle size and composition were deposited on three different carbon supports: Vulcan, graphitized carbon nanofibers (GNF) and few-walled carbon nanotubes (FWCNT) and their performance for methanol oxidation was studied in an electrochemical cell and in a single cell DMFC. The electrochemical results indicate that PtRu/GNF and PtRu/FWCNT result in higher maximum current densities and low poisoning of oxidation intermediates compared to the same catalyst on Vulcan support. Conversely, PtRu/Vulcan provided the highest open circuit voltage OCV and current densities in DMFC experiments due to a well optimized electrode layer structure. However because stability is a key requirement for fuel cell commercialization, also 6 day long fuel cell stability tests showed that PtRu/Vulcan degraded significantly. This was due to the loss in porosity of the electrode layer revealed by post characterization of the membrane electrode assembly MEA with SEM and TEM. PtRu/GNF exhibited slightly poorer initial performance but better stability because the porosity of the anode layer was maintained. PtRu/FWCNT showed the worst initial performance and long term stability. The good stability of non-optimized PtRu/GNF MEAs shows the potential of these novel nanocarbon supported catalysts as stable fuel cell components after proper MEA optimization.

# Graphitized carbon nanofibers as catalyst support for PEMFC

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Vapor grown carbon fibers (VGCF) by Showa Denko are highly graphitized carbon nanofibers with a diameter of 150 nm. VGCFs show superior thermal stability and corrosion resistance in PEMFC environment over traditional carbon black (CB) and carbon nanotube (CNT) supports. However, VGCFs have an inert surface with only very limited amount of surface defects for the anchorage of Pt catalyst nanoparticles. Modification of the VGCF surface is therefore needed. In this study Pt nanoparticles have been deposited onto as-received and surface-modified VGCF under a Nordic cooperation project titled *Synthesis and durability of CNT supported catalysts for PEMFC* (*Nanoduramea*). The surface modifications comprise acid treatment and nitrogen doping by pyrolysis of a polyaniline (PANI) precursor. The modified surfaces were studied by FTIR and XPS. Electrochemical characterization was performed in low temperature PEMFC single cells. The performance of the VGCF supported catalysts are compared with CB supported catalysts and the effects of the different surface treatments are discussed. The Pt/VGCF catalyst shows 5 times lower carbon corrosion than commercial Pt/CB in simulated start/stop cycling with in-situ $CO_2$ monitoring from cathode exhaust.

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# Electrochemical applications of nitrogen-doped carbon nanotubes

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In 2009, Gong et al. [1] found that nitrogen-doped multiwalled carbon nanotubes (N-MWCNTs) efficiently catalyze the oxygen reduction reaction (ORR), free from CO "poisoning" and with a much higher electrocatalytic activity and better longterm operation stability than that of commercially available Pt-based electrodes. This finding has generated immense interest [2] and 180 citations to date. In our contribution, we will review the key literature on the subject, with an emphasis on the proposed mechanisms for the observed reactivity.

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# PrimoLyzer – Pressurized PEM Electrolyzer Stack – Catalyst Development

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Water electrolysis is a verified method for hydrogen production from electric power. Polymer exchange membrane (PEM) water electrolysis is expected to produce hydrogen efficiently and dynamically, particularly for using hydrogen as an energy-storage medium for renewable sources. Oxides of the rutile structure, like $IrO_2$, are typically as anode catalysts because of their high electrocatalytic activity for oxygen evolution in acidic media. Platinum is typically used at the cathode [1]. The primary objective of the PrimoLyzer project is to develop, construct, and test a cost-minimised highly efficient and durable PEM-Electrolyzer stack aimed for integration with PEMFC µCHPs. Catalyst development has important role in this work.

### Anode catalysts

Nanostructured $IrO_2$ and Ir-Ru mixed metal oxides (MMO) have been produced by different wet chemical and aerosol syntheses and characterized by XRD, TEM and electrochemical methods. The results show that Ru addition improves the initial activity of $IrO_2$ for oxygen evolution reaction (OER). The catalysts made by wet chemical methods have been more active than the corresponding catalysts prepared by aerosol methods. However, the aerosol syntheses studied are continuous processesand they would be preferred for production scale up. The activity of the Ir-Ru mixed oxide has been confirmed at MEA level.

### Cathode catalysts

Pt and Pd nanoparticles have been deposited on carbon black (CB) and multi walled carbon nanotubes (MWCNT). The best PtPd/MWCNT catalysts have been 4 times more active than the commercial Pt/CB reference catalyst for the hydrogen evolution reaction (HER).

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# Preparation of CNTs/Au@Pt composite for formic acid electroxiadion

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One of the major barriers for direct formic acid fuel cell commercialization is the high cost and limited abundance of the electrocatalyst. An ions adsorption and subsequent reduction method was employed to prepare the CNTs/Au@Pt electrocatalyst with ultralow Pt loading (0.3 % of the total catalyst mass) while exhibiting high activity and selectivity for formic acid oxidation (see figure 1). Cyclic voltammetry showed that the formic acid oxidation is mainly through dehydrogenation without the formation of CO as a transient specie that causes Pt deactivation. The specific activity was estimated to be 26.6 A•mg$^{-1}$ which shows great potential in formic acid fuel cell application.

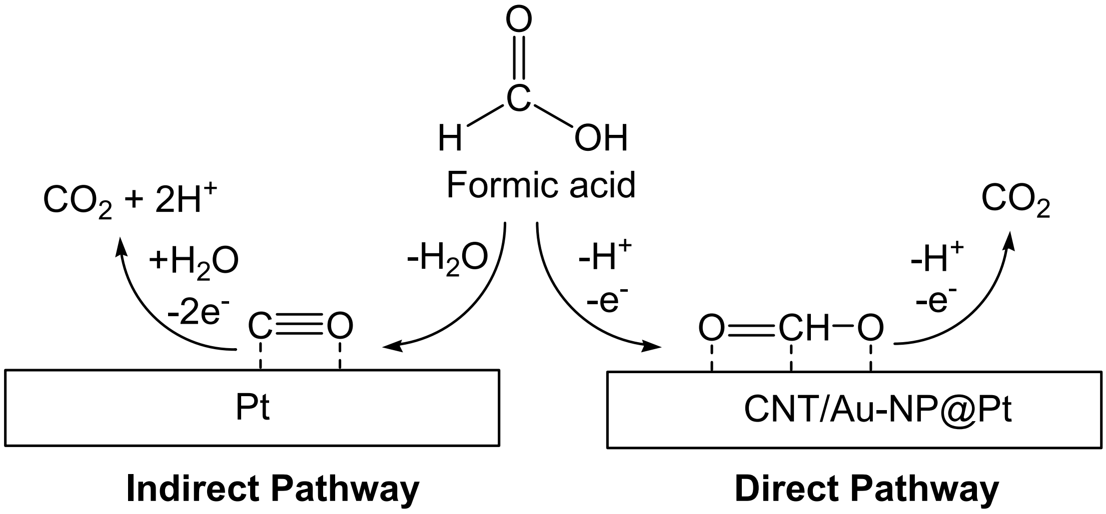

Figure 1. Schematic illustration of formic acid oxidation on Pt and CNTs/Au@Pt.

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# Carbon nanotubes and other nanostructures as support material for nanoparticulate noble-metal catalysts in fuel cells

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In polymer electrolyte membrane fuel cells (PEMFC) a fuel – usually hydrogen – and oxygen are combined to produce electricity and water in an electrochemical process, which is commonly carried out at 60–80 °C. For oxygen reduction and fuel oxidation to occur at such low temperatures platinum or platinum-alloy catalysts in the electrodes are required. To maximize the utilization of the noble metal it is frequently deposited as nanoparticles (1–5 nm) on a stabilizing support of carbon black. Carbon black provides good anchoring of the catalyst particles, but is prone to severe destructive oxidation at high electrical potentials encountered occasionally in fuel cells. Other nanostructures of carbon are being investigated as alternatives to carbon black as they have several beneficial properties. Multi-walled carbon nanotubes (MW-CNT) are an example of one type of these promising materials. Like carbon black they can conduct electrons to and from the reaction sites, and in addition their resistance to electrochemical degradation is better than that of carbon black due to their much higher structural perfection.

This latter feature is indeed highly desired with a view to the durability of the fuel-cell electrodes. However, the low concentration of structural defects also poses challenges with regard to anchoring of the catalyst particles on the CNT surface. Thus, activation treatments introducing surface functional groups may be necessary. Also, the surface properties are responsible for difficulties in contacting the nanotubes with other substances in the electrode or electrode preparation. Other promising candidate structures for catalyst support include carbon nanofibers (CNF) and various modifications of CNTs.

We present some of our work with the investigation of surface properties that are relevant for the preparation of fuel-cell electrodes with increased durability. This includes adsorption studies and studies of the role of the surface structure in the generation of materials-deteriorating reaction intermediates during the electrocatalytic processes.

# Durability of carbon nanofiber & carbon nanotube as catalyst support for PEM fuel cells

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## Introduction

Carbon Nanotube (CNT) and Carbon Nanofiber (CNF) demonstrate huge potentials in fuel cell developments [1, 2]. In this work, thermal and electrochemical durability of CNT and CNF as PEMFC catalyst support were studied and compared to conventional commercial catalyst supports based on both ex-situ and in-situ experiments.

## Experimental and Result

Carbon thermal decomposition properties were tested at 200°C.There is a clear different degradation pattern between CNT / CNF and carbon black. Both CNT and CNF demonstrate less than 10% weight loss, while conventional carbon showed up to 86% weight loss, and Vulcan based catalyst showed over 50% weight loss.

Synergetic degradation between Nafion ionomer and carbon support was studied by thermogravimetry TGA 92-12. There is a synergetic destruction effect between carbon support and Nafion ionomer, since both decomposition temperatures move to lower points. Comparing to Vulcan, CNT & CNF supported catalyst contributes less in Nafion ionomer decomposition, which might be due to the strong hydrophobicity difference; in the mean while, CNT & CNF decomposition is less promoted by the ionomer and catalyst.

Electrochemical stability of the carbon support was also tested with combination of CV acidic media treatment and AAS detection of platinum dissolution [3]. Primary study demonstrated that carbon nanofiber supported Pt catalyst showed much less Pt dissolution especially at high voltage comparing to carbon black supported catalyst.

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# Contamination and Degradation of Perfluorinated Sulfonic Acid Membrane Due to Swelling – Dehydration Cycles

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## Introduction

Formation of sulphuric anhydride S-O-S (from condensation of sulphuric acids) was known one of the important degradation mechanisms [1] for Nafion membrane under hydrothermal aging condition, which is especially critical for hydrogen fuel cells. Similar mechanism would also be desirable to the membrane degradation in direct methanol fuel cells (DMFCs), where liquid water has direct contact with the electrolyte. An ex-situ experiment was established with swelling-dehydration cycles on the membrane. However, formation of sulphuric anhydride was not detected during the entire treatment; instead contamination from calcium was found the primary reason for the deterioration of the membrane properties.

## Experimental and Results

The property changes of commercially available perfluorinated sulphuric acid membrane – Nafion® 212 were continuously monitored during over 60 times swelling (distilled water boil at 1 atm.) – dehydration (vacuum dry, $80^{\circ}$C, 8*10-2Bar) cycles. A combination of weight loss, conductivity, ion exchange capacity, fluoride release, element mapping, thermal stability and different types of microcopies and spectroscopies were applied in the study. Nafion's affinity towards different cations was tested with titration.

The degradation behaviours include decreasing hydrated weight, however increasing dry weight, decreased conductivity and water content, release of fluoride (XPS, and ion selective electrode), almost complete loose of ion exchange capacity etc. SEM topography also illustrates more and more closed surface structure with increasing number of treatment.

Despite only distilled water was used during the treatment, contamination from calcium was confirmed from both EDX element mapping and Raman spectroscopy. Calcium was found forming stable product with sulphuric group, which explains the enhanced membrane thermal property (via thermogravimetry), and also lower water content and consequently lower protonic conductivity.

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# ABSTRACTS
# OF THE POSTERS

## Session II
## Batteries and Basic Nanosciences

# Optical characterization of cu-pva nanocomposite

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The synthesis of the less stable copper nanoparticles is more difficult because copper nanoparticles are easily oxidized. Recently, there have been several reports presenting various approaches which demonstrate that copper nanoparticles can resist oxidation under ambient conditions, if they are coated by a proper protective layer. This layer may consist of an organic polymer, alkene chains, amorphous carbon or graphenes, or inorganic materials such as silica, or an inert metal. In the present work, well dispersed copper nanoparticles were synthesized in Poly vinyl alcohol matrix by reduction of copper nitrate using hydrazine hydrate as a reducer in the presence of NaOH. In this paper, stable metallic copper nanoparticles protected by PVA were prepared in the organic phase. Later with the same solution a film of Cu/PVA was prepared. UV-Visible Spectroscopy was used to characterize both the Cu/PVA solution as well as Cu/PVA nanocomposite film. The characteristic surface plasmon peak has been observed clearly at 585 nm in absorption spectra for the solution and at 606 nm for the film of Cu/PVA nanocomposites. Characterization by TEM shows PVA stabilised Cu nanoparticles. Conductivity measurements and Photoluminescence (PL) of synthesized nanocomposites have been studied. I–V measurements show that with the introduction of copper nanoparticles in PVA its conductivity increases significantly. Possible mechanism for increased conductivity has been discussed.

# Immobilization of pyrroloquinoline quinone on carbon nanotubes

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Pyrroloquinoline quinone (PQQ) is the cofactor of many alcohol or sugar oxidising enzymes, which are candidates for biofuel cells. Because of its fast redox kinetics, it can also be used as a mediator in enzymatic systems, for example with nicotinamide adenine dinucleotide (NAD). It is then vital to study the electrochemistry of PQQ to understand how these enzymes and molecules work in fuel cell applications. However, PQQ does not react readily on metal or carbon electrodes and surface modification and/or immobilization is usually required [1]. In this study, we present a simple way of immobilizing PQQ on carbon nanotubes.

Few-walled carbon nanotubes (FWCNT, diameter 10 nm) were drop-casted on a glassy carbon electrode. Then the electrode was dipped in PQQ solution. After dipping, the electrochemical response of the electrode was studied by cyclic voltammetry. First, the electrode was tested in different pH. The response is strong and reversible over a wide pH range compared to some other techniques [2]. The electrodes were stable in acidic pH and became more unstable in neutral and basic solution. This was probably due to increased negative charge of the FWCNTs. The effect of the pH of the PQQ dipping solution to the amount of adsorbed PQQ was also studied and it was concluded that the highest adsorption happens in low pH (< 2).

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# Controlled growth of multiwall carbon nanotubes on cu and their electrochemical behavior

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Vertically aligned arrays of carbon nanotubes (CNTs) have been recently shown to be advantageous over their randomly entangled counterparts for electrochemical applications, owing to easier accessibility. In particular, improved charge storage / delivery properties are expected for vertically aligned CNTs electrodes thanks to the enhancement of charge transport and ionic diffusion in and through the layer. Moreover, aligned CNTs layers will provide enhanced surface area, and therefore higher capacitance, if a well-defined alignment and a tip-opened structure can be achieved.

In this present work, we investigate the direct synthesis of aligned multiwall carbon nanotubes (MWCNTs) on a copper substrate and their electrochemical behavior. This novel electrode structure can be obtained through a two-step process, namely the electrodeposition of Fe or Co catalyst particles onto the Cu foil and the subsequent growth of MWCNTs by thermal chemical vapor deposition (CVD). Key to a successful development of the process is the ability to control the size and surface coverage of catalyst particles. Accordingly, this is the main objective addressed in our work.

Co or Fe nanoparticles were electrodeposited onto electropolished Cu foils from 0.05 M $Co(NH_2SO_3)_2$ or 0.3 M $Fe(SO_4)_2$, respectively, under various conditions. Right after deposition of the catalyst the Cu substrates were subjected to a thermal pretreatment at 750°C in a mixed working gas ($H_2$ and $N_2$) at varying time. CNTs were subsequently grown by introducing $C_2H_4$ into the gas flow, maintaining the temperature at 750°C during a time interval of 10 min.

The deposition of the catalyst was studied in detail by characterizing the nucleation and growth process of the metal particles on the copper substrate, by both electrochemical methods and morphological examination. The effect of the composition of the electrolyte and of the operating conditions, namely the deposition current density, was examined. Proper conditions for the achievement of an instantaneous nucleation mechanism were defined. The morphology of the catalyst particles was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The morphology and microstructure of the synthesized CNTs layers were characterized by SEM and X-ray diffraction analysis. Transmission electron microscope (TEM) was used to characterize the morphology of the CNTs. The electrochemical capacitance behavior of these novel electrodes was investigated by cyclic voltammetry, galvanostatic charge-discharge studies and electrochemical impedance spectroscopy.

# Design of hybrid active/passive carbon nanotube-based membrane for reverse osmosis water desalination

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The target of the current project is to design a hybrid passive/active Carbon Nanotube (CNT)-based membrane aiming at improving the efficiency and power consumption in Reverse Osmosis (RO) water desalination systems. This shall be achieved by applying external dynamic excitation to the CNT walls using external electrical / electromagnetic driver. This mechanism is expected to improve the permeation properties of vibrating CNT significantly due to the expected flipping of the dipoles of water molecules as a result of wall oscillations that result in significant reduction in the number of Hydrogen bonds inside the nanotube, which eventually allows for easy passage of molecules through the CNT. This investigation shall be carried out numerically using Molecular Dynamics simulation. Along this study, a comprehensive investigation of the mechanical and electrical characteristics of CNTs shall be carried out to optimize the excitation frequency and amplitude to achieve optimal permeation properties and salt rejection.

# Development of lithium ion battery chemicals

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The research on the improvement of lithium ion battery chemicals started in 2010 at the University of Oulu in close co-operation with Aalto University. The co-operative companies cover the whole battery production chain from reactants to the end product. The research is funded by Finnish Funding Agency for Technology and Innovations (Tekes).

The aim of the research is to improve properties of current electrode materials, such as $LiFe_xMn_{1-x}PO_4$-C and $LiCo_yNi_xMn_{1-x-y}O_2$, and to develop new materials. A number of laboratory scale syntheses for lithium ion battery chemicals have been done. Hydrothermal syntheses of $LiFe_xMn_{1-x}PO_4$-C and $LiCo_yNi_xMn_{1-x-y}O_2$ are carried out with an autoclave precipitation. High temperature sintering processes are also used for $LiFe_xMn_{1-x}PO4$-C and $LiCo_yNi_xMn_{1-x-y}O_2$ synthesis. The properties of safe lithium iron phosphate ($LiFePO_4$) are improved by atomic layer deposition (ALD).

Lithium chemicals are characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), differential thermal analysis and thermogravimetric analysis (DTA/TGA), and Mössbauer. These are used for phase identification, grain size measurements and morphological studies, carbon content determination and thermal stability measurements, and on the study of chemical environment of iron, respectively. Electrochemical characterization of the synthesized electrode materials is performed using a battery testing cycler to charge and discharge half-cells in a controlled fashion. The electrodes for the cells are prepared in either wet or dry method. In the dry method, slurry is made by mixing active material, binder, solvent and additives, and finally spread on a metal foil using an applicator. In the wet method the ingredients are mixed in a mortar to a rubbery material, and finally roll pressed into a thin plate. The half cells are assembled in a glove box in Ar-atmosphere to avoid moisture contamination.

Examples of the different characterization studies will be expressed.

# Conductivity of LFP electrodes for Li-ion batteries

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$LiFePO_4$ (LFP) has been considered promising cathode material for lithium ion batteries since its discovery in the 1990s. However, it suffers from poor ionic and electronic conductivity, and there have been several approaches to increase the conductivity, for example by coating the particles with carbon or doping the material with different metals. Substitution of $Fe^{2+}$ with $Mn^{2+}$ in $LiFePO_4$ has been investigated as a method to modify the electrochemical performance of the olivine structure. Mn substitution has been reported to increase the electronic conductivity and electrode kinetics at low Mn contents [1, 2]. However, two-plateau discharge curves have been observed at high Mn content [3, 4].

In this work, electrochemical performance of $LiFe_{1-x}Mn_xPO_4$ was studied with various Mn contents by charge/discharge measurements and cyclic voltammetry. Two-plateau charge/discharge profiles were measured with high Mn contents. Discharge voltage was increased with Mn substitution. Best results were obtained with low Mn content.

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# Electrochemical and Raman-spectroscopic investigations on LCO-material

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$LiCoO_2$ (LCO) tape-cast electrodes are used as cathodes in Lithium-ion batteries. The electrochemical behaviour of such electrodes was investigated in a common half cell with a 3 electrode design as well as in a screw cell with a 2 electrode design (SWAGELOK cell). The latter was used for state of charge (SoC) tests. We carried out electrochemical measurements such as cyclovoltammetry and electrochemical impedance spectroscopy. The electrochemical impedance spectroscopy was carried out depending on the state of charge of the cathode material. The state of charge is associated with the intercalation or de-intercalation of lithium ions within the oxide lattice. Complementary to current controlled charge tests, the samples were investigated by Raman spectroscopy. It can be shown that Raman intensity corresponds to the state of charge of the LCO material. Furthermore, Raman spectroscopy can be used to observe the reversibility of charge or discharge processes and the degradation of material depending on the number of charge cycles.

# Large-format lithium-ion cells – thermal characteristics

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European Batteries Ltd has developed and started a manufacturing facility in Finland for large-format (42 Ah) prismatic lithium-ion cells. Lithium iron phosphate is used as the positive and graphite as the negative electrode material. Large-format lithium-ion battery applications range from transportation to industrial machines and energy storage. Depending on application and ambient conditions the operating temperature of the battery can vary significantly. Thus the cell's thermal characteristics should be studied within a wide temperature range.

In this presentation we concentrate on the thermal characteristics of a lithium-ion cell. Also the cell's technical data and safety features are briefly introduced. The cell performance and impedance are shown as function of temperature. The contributions of ohmic resistance and electrodes' resistance to the overall cell impedance are discussed. A more theoretical aspect of the cell's thermal characteristics is introduced in terms of thermodynamic tests and their results.

Keywords: Li-ion battery, thermal behaviour, cell impedance

# Novel electrode materials for Li-ion battery

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Safety and more efficient materials are the most important issues for a large scale Li-ion battery for applications requiring high power densities, such as electric and plug-in hybrid vehicles. The electrodes of Li-ion batteries are manufactured by coating techniques. The coating method and the binders employed have strong influence on the battery performance.

The present manufacturing process of cathode is expensive, impractical and environmentally unsustainable due to organic solvent needed for the binder material. Our aim is to gain fundamental understanding of the Li-ion battery research starting from material synthesis up to battery performance. This is realized through applying novel electrode and binder materials in our studies.

Our material choices are $Li_4Ti_5O_{12}$ for the negative electrode material and $LiFePO_4$ for the positive electrode material. Both of these are promising materials for use in large scale Li-ion batteries. Their limiting weakness is poor electric conductivity. Solutions for conduction problem are searched from cation doping and conductive additives. Water based binders for electrode manufacturing process will be searched for together with verifying the water tolerance of the active electrode materials $Li_4Ti_5O_{12}$ and $LiFePO_4$.

# $LiFePO_4$ cathode material modified with Carbon nanotubes and surfactant

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Lithium ion batteries have become the most popular rechargeable batteries since available on market because of their high energy density, better safety, good cyclability and portable. Intensive research on electrodes, electrolytes and battery systems has been carried through all over the world, attempted the application for hybrid electric vehicles. In our group the cathode materials based on $LiFePO_4$ were researched for improving the energy density of the Li-ion battery.

Our work aims at improving the performance of cathode materials using carbon nanotubes and surfactant to increase the conductivity of the $LiFePO_4$. The $LiFePO_4$-CNT composites were synthesized by wet chemical method and non-ionic surfactant E-230 was used to modify the dispersion of CNT in the $LiFePO_4$ nano powder. The cathode materials were obtained after sintering at 500–700°C in Ar-$H_2$ air for several hours. The XRD, FESEM and TEM were used for characterization the crystalline phase and microstructure. The charge and discharge performances of Li-ion battery were characterized by coin cell with Li metal electrode. Results showed that the addition of CNT and the surfactant E-230 remarkable increases the charge/discharge specific capacities and more uniform microstructures were observed for the $LiFePO_4$- CNT-E230 composites.

# Printed power source: Supercapacitor with an enzymatic bio-fuel cell

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Inexpensive power sources are needed e.g. in RFID applications. By applying printing techniques the manufacturing costs can be minimized. To widen the applicability range the materials should be easily disposable. Enzymatic bio-fuel cells are an alternative for printable primary batteries. Since bio-fuel cells can provide only relatively low power, we have developed supercapacitors that can be combined with enzymatic bio-fuel cells to facilitate the power peaks demanded in the applications. The materials for the supercapacitors have been chosen to be compatible with the fuel cell and with printing methods, e.g. the activated carbon powder in the electrodes was bound with chitosan. As substrates we have used paperboards and polymer foils. The current collectors have been made of graphite and metal inks. Since the voltage requirement is limited to approximately 1 V, aqueous electrolytes have been used. Supercapacitors of various sizes have been prepared. The geometrical electrode areas have been between 0.5 and 2 $cm^2$. The maximum feasible output current has been in the order of 50 mA corresponding to about 50 mW power. When the capacitor is used together with an enzymatic power source, the leakage current must be as low as possible in order to avoid forming an excess load for the bio-fuel cell. Typical leakage current values have been in the order of 10 μA.

Some general conclusions concerning the electrical properties of supercapacitors have been done. Larger geometrical electrode area leads to lower equivalent series resistance since both the ionic conductivity and electrode conductivity are increased. Also making the activated carbon electrode layer thinner decreases the resistance. The same applies to thinning the separator. The capacitance itself is not dependent on the geometrical electrode area but almost completely on the mass of activated carbon. Leakage current depends also on the geometrical area but in some cases it seems to be even more dependent on capacitance and thus the activated carbon surface area. The majority of the leakage current is probably consumed to maintain the double layer.


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# Eicoon Workshop and Summer School
## Nanomaterial Issues in Electrochemical Energy Conversion: Fuel Cells, Batteries, Supercapacitors

Abstract

The Euro-Indo forum for nano-materials research coordination & cooperation of researchers in sustainable energy technologies (EICOON) project has addressed the nano-materials research and training needs and mutual research interests in the EU and India and communicated them to the European Commission (DG RTD) and Indian Government (DST). In addition, the EICOON project organizes events for researchers to exchange their research results and ideas. The EICOON workshop and summer school “Nanomaterial issues in electrochemical energy conversion: fuel cells, batteries and supercapacitors” organized by VTT Technical Research Centre is part of scientific seminars and thematic summer schools within the project.

100 European and Indian scientists gathered together on June 13–17, 2011 to Otaniemi, Espoo, Finland for this networking event. 30 invited oral presentations were giving by leading European and Indian nanomaterial researchers and electrochemists and 22 student posters were given in the summer school.

The project and workshop funding by European Commission under the contract 233466 is gratefully acknowledged.

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