

# SYMPOSIUM E

## Electrochromic Materials and Applications

November 29 - 30, 2005

### Chairs

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\* Invited paper

**8:30 AM \*E1.1**

**Hydrogenography: combinatorial search of new electrochromic materials.** Ronald Griessen, Bernard Dam, Andreas Borgschulte, Robin Gremaud, Philippe Mauron, Herman Schreuders and Martin Slaman; Physics/Faculty of Sciences, Vrije Universiteit, Amsterdam, Netherlands.

Hydrogenography is a novel technique based on the optical changes induced by hydrogen ab- and desorption in metal films. Hydrogenography on thin films with a compositional gradient has the great advantage that it makes it possible to measure simultaneously a huge number of samples (effectively up to thousands) of different elemental compositions on only one wafer (each pixel of the recording camera corresponds essentially to one alloy composition). This enormously facilitates the search for new (complex) metal-hydrides with specific switchable physical properties. The compositional gradient thin films necessary for hydrogenography are synthesised by co-sputtering on a 3 in wafer from three (up to six) off-centred magnetron sources. The (complex) hydride formation during ex-situ hydrogen exposition at well-defined temperatures and hydrogen gas pressures is monitored by the transparency/reflection of the films. Since all complex hydrides found so far have an electronic bandgap their transparency is a good indicator of the amount of absorbed hydrogen. Hydrogenography is thus applicable to a large class of potential light-weight hydrogen storage materials and electrochromic materials. As an illustration of our new technique I describe how hydrogenography is used to optimize so-called black switchable mirrors [1]. These are thin layer materials that exhibit a reversible transition between shiny metallic (without hydrogen) and a strongly absorbing (black) state at moderate hydrogen content. Such materials offer interesting possibilities for applications as fiber optic hydrogen sensors, solar collectors and variable reflectance rear-view mirrors. We have obtained interesting results for the Mg-Ni-Co-H and Mg-Ni-Fe-H systems. They show that the hydrogen absorption as well as the kinetics of hydrogenation depends strongly on the local elemental composition since during hydrogenation various well-defined and well-separated transparent regions appear at specific elemental compositions. Hydrogenography is also of great help in the search and optimisation of the catalytic layer covering the switchable mirror material [2]. 1. W. Lohstroh, R. J. Westerwaal, B. Noheda, S. Enache, I. A. M. E. Giebels, B. Dam, and R. Griessen: Self-organized layered hydrogenation in black Mg<sub>2</sub>NiHx switchable mirrors, Phys. Rev. Lett. 93 197404 (2004) 2. A. Borgschulte, R. J. Westerwaal, J. H. Rector, B. Dam, R. Griessen, and J. Schoenes: The effect of the Strong Metal-Support Interaction on hydrogen sorption kinetics of Pd-capped switchable mirrors, Phys. Rev. B 70, 155414 (2004)

**9:00 AM E1.2**

**Optical Switching Properties of All-solid-state Switchable Mirror Devices Using Magnesium-nickel Alloy Thin Film.** Kazuki Yoshimura, Shanhu Bao, Yasusei Yamada and Masahisa Okada; MRSUS, AIST, Nagoya, Aichi, Japan.

All-solid-state switchable mirror devices using Mg-Ni alloy thin film were prepared by magnetron sputtering and their optical switching properties have been investigated. The structure of the devices is Mg-Ni alloy/Pd/Ta<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/ITO on glass substrates. The typical composition of the alloy is Mg<sub>4</sub>Ni. WO<sub>3</sub> layer is colored into blue state before Pd and Mg-Ni depositions by *insitu* coloration with introducing H<sub>2</sub> gas during sputtering or *exsitu* electrochemical coloration by using acid solution. An indium piece is used for glue of electric wire to the outermost Mg-Ni layer. When a voltage of +6V is applied between ITO (positive pole) and Mg-Ni layer (negative pole), the optical transmittance of the device increases and turns to be the transparent state from the metallic state. The applying voltage of -6 V causes the reverse transition from the transparent state to the metallic state. We prepared each layer with various conditions and observed their optical switching properties, resulted our new findings that the devices can be categorized into two types. Type I: The transition from the metallic state to the transparent is fast (about 10 seconds) in the vicinity area ( $\approx 1 \text{ mm}^2$ ) of indium electrode. However, the transparent area spreads very slowly from the electrode. It takes about 1 hour for the whole change in  $1 \text{ cm}^2$  area. Type II: The transition speed from the metallic state to the transparent state is not so fast compared with that of Type I device. However, this change occurs in wide area uniformly. These two types of devices can be prepared by controlling the preparation condition of Ta<sub>2</sub>O<sub>5</sub> layer. In the type I device, Ta<sub>2</sub>O<sub>5</sub> layer contains considerable amount of water. On the contrary, Ta<sub>2</sub>O<sub>5</sub> layer contains little amount of water in the type II device. The difference of water content affects the proton diffusion into Mg-Ni layer. Type I device is suitable for small optical switching device such as a fiber-optic switch, while type II device is suitable for large area switchable glazing such as a smart window.

**9:15 AM E1.3**

**Progress Toward an Electrochromic Switchable Mirror.** Thomas Richardson, Jonathan Slack, Jan Isidorsson, Oliver Meier and Brenden Millstein; Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California.

A new generation of electrochromic windows that control both visible and infrared transmission and reflection will lead to increased energy savings and user comfort. Several different materials systems have been investigated by the LBNL Chromogenic Materials Group. For the past two years we have been developing a prototype electrochromic window based on transition metal-magnesium alloy films that convert from a highly reflective state to a color neutral transparent state by reaction with hydrogen. The novel design uses the insulating gas fill to store hydrogen for switching the active electrode rather than an ion storage layer. This reduces the number of thin film layers required and the overall thickness and absorbance of the stack, while ensuring the availability of sufficient hydrogen for many years of operation. A progress report on development of the solid state electrolyte and other components will be presented.

**9:30 AM E1.4**

**Optical Properties of MgyTM (TM=Ni, Co, Fe) Hydrides.** A. C. Lokhorst<sup>1</sup>, W. Lohstroh<sup>2</sup>, H. Schreuders<sup>1</sup>, B. Dam<sup>1</sup> and R. Griessen<sup>1</sup>; <sup>1</sup>Solid State Physics, Vrije Universiteit Amsterdam, Amsterdam, Netherlands; <sup>2</sup>Forschungszentrum Karlsruhe GmbH, Karlsruhe, Germany.

MgyTMHx (TM=Ni, Co, Fe) thin films can be used as switchable mirrors, since their optical appearance changes upon hydrogen uptake [1]. The reflecting metallic Mg-TM films change into transparent semi-conductors during hydrogenation. In between, a third, absorbing state is observed [2]. These metal-hydrides can be switched by an applied hydrogen gas pressure, but can also be hydrided electrochemically, enabling integration in an all-solid-state device. We present the optical properties of both the fully hydrided and the intermediate black states. The fully hydrided MgyTM (2<y(6) thin films are investigated at photon energies between 0.2 and 5.5 eV. All films show the characteristic absorption bands in the infrared, increasing with decreasing Mg-content. Hence we conclude that indeed the complex magnesium transition metal hydrides are formed upon hydrogenation. The transmission increases with increasing Mg-to-TM ratio, while the transmission edge shifts to higher energies. The dielectric function of the hydrided samples is determined from transmission and reflection measurements. They depend on the Mg-content, but cannot be modelled as a simple mixture of MgyTMHx and MgH<sub>2</sub>. Besides the fully hydrided state, we investigated the optical behaviour during hydrogenation. The absorbing nature of MgyNiHx is essentially an interference effect due to a self-organized double layering. The MgyNi-hydride layer nucleates at the substrate interface and grows on hydrogenation at the expense of the upper metallic MgyNi layer. Only for TM=Ni does a binary Mg-TM parent alloy exist with the same composition as the ternary Mg<sub>2</sub>TMHx. This is not the case for TM=Co and Fe. We found that the hydrogenation behaviour of Mg-Co and Mg-Fe alloys depend on the hydrogen loading cycle. In subsequent cycles, the hydrogenation changes from a mainly homogeneous nucleation to a more double-layer like behaviour. This change in loading behaviour increases with the Mg content. It is probably caused by an atomic redistribution resulting in a better mixture of the Mg and TM. This is confirmed by the disappearing Mg (002) and (004) peaks in X-ray diffraction measurements. Also, the microstructure might play a role as observed by SEM. In conclusion, we find that both the optical properties of the fully loaded state as well as the hydrogenation process of Mg-TM (TM=Ni, Co, Fe) depend strongly on the Mg-content. 1. T.J. Richardson, J.L. Slack, B. Farangis, and M.D. Rubin, **Mixed metal films with switchable optical properties**, Appl. Phys. Lett., **80** (8), 1349-1351 (2002) 2. W. Lohstroh, R.J. Westerwaal, B. Noheda, S. Enache, I.A.M.E. Giebels, B. Dam, and R. Griessen: **Self-organized layered hydrogenation in black Mg<sub>2</sub>NiHx switchable mirrors**, Phys. Rev. Lett. **93** 197404 (2004)

**9:45 AM E1.5**

**Room temperature opto- and electro-sensing of hydrogen based on Magnesium-Nickel switchable mirrors.** Bruno Meyer<sup>1</sup>, Baker Farangis<sup>1</sup>, Dietmar Hasselkamp<sup>1</sup>, Jennifer Stiebich<sup>1</sup>, Claus-Dieter Kohl<sup>2</sup> and Cathrin Mucha<sup>2</sup>; <sup>1</sup>Physikalisches Institut, Giessen, Germany; <sup>2</sup>Institut fuer Angewandte Physik, Giessen, Germany.

The hydrogen sensing property in nickel magnesium alloy film is reported. Pd-capped Ni-Mg thin films prepared on special sensor substrate by RF sputtering have metallic behaviour in air. An increase of ohmic resistance upon exposure to hydrogen gas is observed at room temperature. The work function measurements for optosensing have been carried out by means of a photoelectric barrier.

For this purpose the films were sputtered on glass substrate. An infrared emitter (GaAs) was used as light source. During hydrogenation the voltage of silicon NPN phototransistor (detector) was recorded. The response time is very fast and the saturation level, because of hydrazination and dehydrazination is stable. Due to those properties, these films are supposed to be candidates for low-cost room temperature hydrogen sensor.

SESSION E2: Polymers for Electrochromics I  
Chair: Thomas Richardson  
Tuesday Morning, November 29, 2005  
Room 305 (Hynes)

#### 10:30 AM \*E2.1

**Electrochromic Devices Based on Hydrophobic Ionic Liquids.** Marie-Helene Delville, Guy Campet, Sandrine Duluard, Isabelle Litas and Hyun Jung; Chemistry, Institut de Chimie de la Matiere Condensee de Bordeaux, Pessac, France.

Electrochromic devices (ECD) are, along with suspended-particle devices (SPD), one of the two most popular technologies in the area of light control. Both technologies are being developed for buildings and automotive windows, as well as mirrors. We will report here on the development of large area ECD which advantageously use hydrophobic lithium electrolytes, as an alternative to more classical non-aqueous and hygroscopic lithium electrolytes. We propose the use of hydrophobic ionic liquids-based electrolytes because (i) the ionic liquids allow the manufacturing of the devices in ambient atmosphere and (ii) they possess highly attractive intrinsic properties: non-volatility, non-flammability, high ionic conductivity and non-toxicity. We have tested the compatibility of these electrolytes with various electrochromic electrode materials, prepared either by sputtering, sol-gel process, electrodeposition, such as  $\text{WO}_3$ ,  $\text{Li}_{0.5}\text{Ni}_{0.50}\text{O}$ ,  $\text{Li}_{0.5}\text{Cr}_{0.50}\text{O}_{1.25}$ ,  $\text{Fe}_2\text{O}_3$ , Prussian Blue, PANI. The major requirement for the inorganic oxides is to be amorphous or polycrystalline with a grain size as small as possible. Indeed, by minimizing the size of the crystallites the formation of defect bonds is favoured, particularly at the crystallite surface, acting as reversible (de) grafting sites of  $\text{Li}^+$ . The electrochemical cycling of the ECD, using 1-ethyl-3-methylimidazolium bis-trifluoromethane sulfonimide as ionic liquid, shows reversible cycling even at elevated temperature (up to  $100^\circ\text{C}$ ). Moreover the long term (over several years) chemical stability is also reported.

#### 11:00 AM E2.2

**Ionic transport in conjugated polymer films measured via electrochromism.** Nathaniel D. Robinson, Joakim Isaksson, David Nilsson and Magnus Berggren; Dept. of Science and Technology (ITN), Linköping University, Norrköping, Sweden.

Electrochemical polymer devices, from transistors and displays to light-emitting cells all require both electron and ion transport to function. Although electronic conduction in conjugated polymers is many orders of magnitude smaller than in metals, it is often the ion transport that limits device functionality. Understanding this transport allows both for the improvement of current device speed and for the creation of devices that take advantage of the transport limitation and/or differences in transport between ionic species. The manner in which lateral electrochromic devices switch can be used to measure the rate of transport of the limiting species. Simple structures are created from polymer films and liquid or semi-solid electrolytes to demonstrate limitation by electron transport and ion transport, depending on the choice of polymer and electrolyte. This technique is extended, employing both the charge transport (electronic current) measured and the electrochromic switching of the polymer, to measuring the rate of transport of different species of ions within the polymer film itself.

#### 11:15 AM E2.3

**Electrochemical Behaviour of Tungsten Oxide ( $\text{WO}_3$ ) and Prussian Blue (PB) Films in Various Electrolytic Media Including Ionic Liquids.** Sandrine Duluard, Isabelle Litas, Hyun Jung, Guy Campet and Marie-Helene Delville; Chemistry, ICMCB, Pessac, France.

Complementary tungsten oxide ( $\text{WO}_3$ ) and Prussian blue (PB) electrochromic devices (ECDs), in combination with  $\text{Li}^+$ ,  $\text{K}^+$  or  $\text{H}^+$ -based electrolytes, have been proposed by many researchers for Electrochromic devices (ECD). In this study, cycling performances of ECD comprised of  $\text{WO}_3$  and PB thin films coupled with hydrophobic lithium-conducting electrolytes are discussed. For some devices, the transmittance varied from 70% to 10.0% at 600 nm. The device was darkened or bleached by the application of 0.6 V. Repeated switching or cycling of the ECD over 1,000 cycles has been demonstrated, without noticeable degradation.

#### 11:30 AM E2.4

**Electrochromic properties of polyABTS-ITO prepared via layer-by-layer deposition.** J. Fei<sup>1</sup> and G. T. Palmore<sup>1,2</sup>;

<sup>1</sup>Engineering, Brown University, Providence, Rhode Island; <sup>2</sup>Biology and Medicine, Brown University, Providence, Rhode Island.

The molecule, 2,2-azino-bis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS), is an important redox-active compound with chemical, materials, and biomedical applications. ABTS and its derivatives have been used as the electrochromic component in smart windows, as a chromogenic substrate in biochemical assays, and as a mediator for electron transport in bioelectrocatalysis. Devices made with monomeric versions of an electroactive compound often lack long-term stability because of losses due to leaching. As such, polymeric versions of electroactive compounds are desirable as it eliminates leaching and also improves overall adhesion of the material to the underlying substrate. In this talk I will discuss the synthesis and characterization of the first polymerizable derivatives of ABTS. A layer-by-layer technique was used to deposit the resulting hydrophilic polymer of ABTS with polyethylenimine onto an ITO substrate. The electrochemical behavior and the electrochromic properties (e.g., response time, contrast, and stability) of the resulting assembly will be presented.

#### 11:45 AM E2.5

**Additive Primary Colors in Polymeric Electrochromics.**

Gursel Sonmez<sup>1</sup>, Hayal B. Sonmez<sup>2</sup>, Clifton K. F. Shen<sup>2</sup> and Fred Wudl<sup>2</sup>; <sup>1</sup>Faculty of Engineering & Natural Sciences, Sabanci University, Istanbul, Turkey; <sup>2</sup>Department of Chemistry and Biochemistry and Exotic Materials Institute, University of California, Los Angeles, Los Angeles, California.

The ability to have three complementary colors, red, green and blue constitutes an important step forward for the use of conducting polymers (CP) in polymeric electrochromic devices. As these three legs of color space are completed, all other colors can be obtained according to color mixing theory. Recently, we have initiated a study to obtain a CP which reflects the absent green light in the neutral state and is transparent in the oxidized state. We believed that the goal could be achieved with the synthesis of a polymer backbone containing two well-defined, conjugated systems which absorb blue (>600 nm) and red (<500 nm) colors. With this in mind, a 2,3-di(thien-3-yl)-5,7-di(thien-2-yl)thieno[3,4-b]pyrazine (1) monomer that would afford two conjugated chains was designed and synthesized. Electrochemically prepared poly(1) showed high green color saturation, fast switching property and extreme stability that makes this material promising for completion of the deficient third leg of the color space and also opens the way to fabricate polymeric RGB electrochromic devices.

SESSION E3: Inorganic Electrochromics

Chair: Franco Decker

Tuesday Afternoon, November 29, 2005

Room 305 (Hynes)

#### 1:30 PM \*E3.1

**Electrochromic Glazings for the Automobile Industry.**

David Pender and Jean-Christophe Giron; Saint Gobain Sekurit, Herzogenrath, Germany.

In newer automobiles there is a constant trend towards the use of more glass in the car body. Panoramic sunroofs, either as single or multiple piece roofs, give an amazing feeling of openness and freedom, and are a more comfortable alternative to carbios. Electrochromic glazings allow the end-user to maintain these positive feelings without experiencing some of the negatives associated with the extra energy transmission, sometimes associated with larger sunroofs. This presentation will talk about Electrochromic sunroofs and will include a description of the first ever serial production of a laminated electrochromic sunroof for the automobile industry.

#### 2:00 PM E3.2

**Environmental Rating of an Electrochromic Glazing.** Eleni Syrrakou, Spiros Papaefthimiou and Panayiotis Yianoulis; Physics Department, University of Patras, Solar Energy Lab, Rion - Patras, Achaia, Greece.

It is well known that the building sector has a significant contribution to the consumption of energy and to associated environmental impacts, such as greenhouse gas emissions, toxic air emissions, etc. In accordance with the European Directive on the energy performance of buildings, the reduction of the cooling and heating energy consumption is both an environmental and economical concern. Advanced glazing can have a significant role towards this direction. A considerable development has been performed during the last decades

by providing consumers with fenestration products having improved properties and being suitable for various climatic conditions and building use. Electrochromic (EC) glazing can combine solar and visual transmittance control and reduce energy demands in buildings. A 40 cm × 40 cm prototype EC device (K-Glass/WO<sub>3</sub>/electrolyte/Li<sub>y</sub>V<sub>2</sub>O<sub>5</sub>/K-Glass) was used as the reference case in this study. The energy savings derived from its implementation in a building have been evaluated and compared with the corresponding values of various Insulating Glass Units. The environmental profile of the devices was identified combining suitable eco-efficiency indicators and the Life Cycle Assessment (LCA) methodology based on ISO 14040. The energy balance was estimated to assess the energy saving potential and the contribution to the reduction of greenhouse gas emissions and human toxicity through the air. Scenarios of improved control strategies of EC devices implemented in a building located in the three climatic areas of Greece have been analyzed, assuming a lifetime ranging between 10-25 years. It was found that the building energy needs can be reduced by almost 56% when the EC device is used in cooling dominated areas. More than 30 MJ are saved per MJ consumed during its lifecycle, the corresponding CO<sub>2</sub> emissions reduction is more than 480 kg CO<sub>2</sub> equivalent, while the reduction in human toxicity emissions through the air can reach the 46 kg 1,4-DCB equivalent, when its lifecycle is extended to 25 years. If the lifecycle is extended above 20 years and the device price is reduced to 200 —\*euro\*/m<sup>2</sup>, each MJ saved would cost less than the current electricity price (1.07 euro cent/MJ). The above results indicate the high environmental performance of the EC glazing, their environmental benign nature and enhance their use as energy saving devices of the building envelope, while the reduction in purchase cost and the increase of lifetime are the two main future targets. Significant issues for decision-making purposes in the product design and development arise from the combination of the two methodologies (eco-efficiency and LCA). Thus the optimum balance of the EC glazing properties and the selected control strategy can be identified for specific areas/climates. Furthermore, the results of such an analysis can be helpful for the environmental rating of various fenestration products.

### 2:15 PM **E3.3**

**Solid State Electrochromic Films and Devices Produced by Plasma Enhanced Chemical Vapor Deposition.** Mike Seman<sup>1</sup>, Wenli Yang<sup>1</sup>, Joshua J. Robbins<sup>2</sup> and Colin A. Wolden<sup>1</sup>; <sup>1</sup>Chemical Engineering, Colorado School of Mines, Golden, Colorado; <sup>2</sup>CMD Research, LLC, Golden, Colorado.

Electrochromic thin films are most commonly fabricated by physical vapor deposition (PVD) techniques such as sputtering and evaporation. Our group has developed plasma enhanced chemical vapor deposition (PECVD) as an alternative approach to transition metal oxides synthesis for electrochromic applications. This talk will focus on thin film device structures that employ tungsten oxide, vanadium oxide, and tantalum oxide as the electrochromic, ion storage, and electrolyte, respectively. In each case the deposition rate and film properties were optimized as a function of plasma parameters. Ion storage and transport were quantified in a standard 3-electrode electrochemical configuration with a number of approaches including potentiostatic and galvanostatic intermittent titration techniques. Spectrophotometry and spectroscopic ellipsometry were used to characterize the films' optical response. In each case PECVD delivered commercially viable deposition rates at room temperature that were up to an order of magnitude greater than values typically reported for conventional PVD technology. In addition, the electrochemical performance could be optimized within this range. Tungsten oxide was deposited using mixtures of WF<sub>6</sub>, H<sub>2</sub>, and O<sub>2</sub>. For WO<sub>3</sub> it was found that film density and performance were sensitive to the plasma operating conditions. By tailoring the degree of ion bombardment diffusion coefficients of 10-9 and 10-10 cm<sup>2</sup>/s were obtained for H<sup>+</sup> and Li<sup>+</sup>, respectively. Vanadium oxide was deposited using VOCl<sub>3</sub> as a precursor, and unlike WO<sub>3</sub>, it was found that hydrogen was not required to produce high quality material. The electrochemical performance of V<sub>2</sub>O<sub>5</sub> films was found to be robust with respect to plasma conditions, and Li<sup>+</sup> diffusion coefficients as high as 10-11 cm<sup>2</sup>/s were obtained. In addition, the optical band gap of V<sub>2</sub>O<sub>5</sub> increased with lithium ion intercalation from 2.1 eV in as-deposited films to 3.15 eV at high ion storage levels. Our current work is examining the deposition of Ta<sub>2</sub>O<sub>5</sub> as a solid-state electrolyte using Ta(OCH<sub>2</sub>CH<sub>3</sub>)<sub>5</sub> and O<sub>2</sub>. The Ta<sub>2</sub>O<sub>5</sub> deposition rate and material properties are examined as a function of plasma parameters. In addition to the intrinsic properties of individual films, we explore integration issues and report on the performance of multi-layer half cell and complete electrochromic devices.

### 3:30 PM **\*E3.4**

**Electrochromics for Smart Windows: Thin Films of Tungsten Oxide and Nickel Oxide, and Devices Based on These.** Claes G. Granqvist and Gunnar A. Niklasson; Department of Engineering Sciences, The Angstrom Laboratory, Uppsala University,

Uppsala, Sweden.

We briefly review recent literature on inorganic electrochromic materials and point at today's emphasis on W oxide (with cathodic coloration) and Ni oxide (with anodic coloration). The properties of thin films of these materials are then discussed in detail with foci on recent results from comprehensive investigations in the authors laboratory. The exposition covers, in sequence, structural features, thin film deposition (by sputtering), electronic band structure, and ion diffusion. For W oxide we mention a novel, conceptual model for the structural characteristics of amorphous films based on notions of defects in the ideal amorphous state. It is shown that the conduction band density of states can be obtained from electrochemical chronopotentiometry. Upon ion intercalation, the charge-compensating electrons enter these localized states, implying that the optical absorption underlying the electrochromism can be described as due to transitions between occupied and empty localized conduction band states. The optical absorption is modelled, phenomenologically, as due to a superposition of transitions between different charge states of the tungsten ions (6+, 5+, 4+). The Ni oxide films were found to have a porous structure with small grain size. Electrochromic coloration is described as a surface phenomenon, most likely confined to the outer parts of the grains. Initial electrochemical cycling transformed hydrated Ni oxide to hydroxide and oxy-hydroxide phases on the grain surfaces. Electrochromism in thus stabilized films is consistent with reversible changes between Ni hydroxide and oxy-hydroxide, in general accordance with the Bode scheme. An extension of this model is put forward to account for changes of NiO to Ni<sub>2</sub>O<sub>3</sub>. It is demonstrated that electrochromism is associated solely with proton transfer. Data on chemical diffusion coefficients are interpreted, both for polycrystalline W oxide and Ni oxide, in terms of the lattice gas model with interaction. The later part of this presentation is of a more technological and applications-oriented character and departs from the fact that that electrochromic devices with large optical modulation range can be accomplished by connecting W-oxide-based and Ni-oxide-based films through a purely ion-conducting layer. Specifically, we cover methods to enhance the bleached-state transmittance by mixing the Ni oxide with other oxides characterized by wide band gaps, and we also discuss pre-assembly charge insertion and extraction by facile gas treatments of the films, as well as practical device manufacturing and device testing. The emphasis is on novel flexible polyester-foil-based devices. The final part of the presentation deals with applications to architectural "smart" windows capable of achieving improved indoor comfort jointly with significant energy savings due to lowered demands for space cooling. We also touch upon applications to eyewear.

### 4:00 PM **E3.5**

**Formation mechanism and physico-chemical properties of mesoporous crystalline thin films of tungsten oxide.** Bernd Smarsly and Torsten Brezesinski; Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

The scaling down of metal oxides to the nanometer scale has attained significant attention, because their inherent physical properties (electrochromism, photocatalysis, etc.) are expected to be improved due to the high surface area, which is advantageous for any application based on exchange with matter, e.g. electrolytes. WO<sub>3</sub> is well-known for its electrochromic behavior, which could be of significant technological importance in the form of switchable coatings on windows, mirrors, etc., but current devices suffer from slow response times. In the present study, for the first time crack-free mesoporous WO<sub>3</sub> films were fabricated, possessing a highly crystalline, pure-phase scaffold with nanocrystallites of ca. 10-15 nm and spherical mesopores of ca. 10 nm in diameter. The final films feature an internal surface area of ca. 200 m<sup>2</sup>/g. Our approach involved dip-coating of polar substrates (e.g. glass) by an ethanolic solution of a hydrolysable tungsten oxide precursor and special structure-directing agents such as amphiphilic block copolymers of the KLE-type.[1] Subsequently, the films were heat treated in air by a well-defined ramp (1-5 deg C/min) to initiate and control crystallization of the amorphous tungsten oxide matrix, leading to a final, tunable film thickness of 10-1000 nm. The crystallisation behavior and the mesostructural evolution upon temperature treatment were studied in detail by in-situ small- and wide-angle X-ray scattering, electron microscopy (TEM, HRTEM, SAED), AFM and XPS. In order to investigate their electrochromic behavior, WO<sub>3</sub> films were prepared on glass substrates covered with fluor-doped tin oxide conducting layers, using LiClO<sub>4</sub> in poly(ethylene glycole) as electrolyte. Cyclic voltammetry experiments showed a completely reversible oxidation/reduction over at least 1000 cycles. The optical transmittance of the films was studied as a function of the applied voltage for several wavelengths in the visible region, compared to non-porous and amorphous tungsten oxide materials, prepared under similar conditions. These studies revealed a positive influence of the mesoporosity on the switching times; both the coloration and bleaching of the films occurred on a time-scale of less than a second, while non-porous crystalline thin films showed

response times of more than 10 seconds. The positive influence of the mesoporosity can be attributed to the facilitated diffusion of the electrolyte towards the WO<sub>3</sub> nanocrystallites in the walls separating the mesopores. Hence, our study clearly proved that the introduction of mesoporosity significantly improves the electrochromic response times of WO<sub>3</sub> coatings. Since the preparation method is applicable to any polar substrate, our results suggest a methodology for a substantial enhancement of the performance of WO<sub>3</sub> coatings in technical applications. [1] Smarsly et al. Chem. Mater. 2004, 16, 2948.

#### 4:15 PM E3.6

##### Optically passive (CeO)<sub>x</sub>(TiO)<sub>1-x</sub> and (FeO)<sub>x</sub>(TiO)<sub>1-x</sub> counter-electrodes prepared from surfactant solutions.

Boris Orel, Angela Surca Vuk, Dasa Sivec, Ivo Jerman, Robi Jese and Lidija Slemenik Perse; Laboratory for Spectroscopy of Materials, National Institute of Chemistry, Ljubljana, Slovenia.

Electrochromic (EC) devices have been extensively investigated in the past due to their potential application as smart windows for buildings. For smart glazing in particular, high transmittance of the EC device in the bleached state is desired. This desire has instigated the development of counter-electrodes which show only a small variation in their transmission during the intercalation/deintercalation reactions. Since the counter-electrode remains transparent during cycling, the reversible coloration and bleaching reactions of the EC device rely solely on the electrochromic properties of the active electrode (usually WO<sub>3</sub>). This sets up severe conditions for the counter-electrode performance, i.e. a high charge capacity combined with an optical modulation of less than 5%. (CeO)<sub>x</sub>(TiO)<sub>1-x</sub>, one of the first studied counter-electrodes of this kind, exhibits stable charge capacities in the range 10-15 mC/cm<sup>2</sup>. A characteristic feature of its structure is that cerianite nanoparticles are embedded in the amorphous TiO<sub>2</sub> host. Various precursors for cerium oxide have been used for the preparation of (CeO)<sub>x</sub>(TiO)<sub>1-x</sub> mixed oxide films, while Ti(OiPr)<sub>4</sub> has been used as a source of titanium oxide. We have opted to make (CeO)<sub>x</sub>(TiO)<sub>1-x</sub> films by adopting the synthesis procedure usually employed for the preparation of nanocrystalline TiO<sub>2</sub> films from surfactant solutions. Various surfactant solutions were tried, with Pluronic F-127 found to be optimal in combination with a solvent, acetic acid catalyst, Ti(iPrO)<sub>4</sub> and cer(IV) ammonium nitrate precursor. The structure of films was investigated using XRD, TEM and AFM techniques and the results combined with IR and Raman spectroscopic measurements. With the help of IR transmission spectra measurements of films under high vacuum conditions, surface hydroxyl (isolated, vicinal) groups were determined together with Lewis and Brønsted acids sites. It was found that the TiO<sub>2</sub> films contained more surface hydroxyl groups than the (CeO)<sub>x</sub>(TiO)<sub>1-x</sub> films. Electrochemical studies were started with an assessment of the  $V_{OC}$  (LiOH, LiClO<sub>4</sub>/PC electrolytes), which showed a variation with time of equilibration. The charge capacities of the (CeO)<sub>x</sub>(TiO)<sub>1-x</sub> films made with surfactants were higher than those of the films made without them and were about 12 mC/cm<sup>2</sup> for films of 150 nm in thickness. Identical studies to those performed for (CeO)<sub>x</sub>(TiO)<sub>1-x</sub> films were also carried out for (FeO)<sub>x</sub>(TiO)<sub>1-x</sub> films. It was found that the latter films outperformed (CeO)<sub>x</sub>(TiO)<sub>1-x</sub> films, exhibiting charge capacities above 20 mC/cm<sup>2</sup> and high (>500 cycles) cycling stability in LiOH electrolyte. In addition, both films were studied with the help of in-situ and ex-situ spectroelectrochemical IR techniques, which enabled the establishment of the reaction products formed over the course of the prolonged electrochemical cycling.

#### 4:30 PM E3.7

##### Enhancement of Electrochromic Properties of Electrochemically Fabricated Mesoporous Nickel Oxide Thin Films. Takako Yoshino and Yoshinari Misaki; Tokyo Metropolitan University, Hachioji, Japan.

We have electrochemically fabricated of mesoporous nickel oxide thin films by utilizing a surfactant assembly under a controlled potential range, in order to improve the electrochromic properties. The films were potentiostatically electrodeposited from a solution of 10mM Ni(NO<sub>3</sub>)<sub>3</sub> containing 0.1wt% sodium dodecyl sulfate(SDS) surfactant, at room temperature without stirring the solution and under a potential range from ?1.0V to ?0.7V. The films obtained were washed with pure water and ethanol to remove the remaining surfactant and dried in air. Characterizations of the films were made by using TEM and XRD. The electrochromic behaviors of the films were measured by cyclic voltammetry, where a glassy carbon and Ag/AgCl electrodes were used as a counter and reference electrode respectively. The XRD patterns showed that the fabricated film at ?0.8V periodical patterns in the small angle region. The result suggests that a high ordered structure is present in the film. The deposition potential exerts a great influence on the SDS assembly and mesoporous structure of the film. Transmission electron microscopy (TEM) image show the lamellar mesoporous structure in the film deposited with SDS at ?0.8V. In the previous paper, we reported that we fabricated mesoporous lamellar structure of Ce-Co mixed oxide films and nanotubes of Co(OH)<sub>2</sub>

films, and confirmed of their enhancement of electrochromic properties. In this paper, the evaluation of the electrochromic properties of mesoporous lamellar nickel oxide films has been made.

#### 4:45 PM E3.8

##### Enhanced electrochromic properties for Ni-M-O (M = Co, Ta, W) thin films. Nicolas Penin<sup>1</sup>, Aline Rougier<sup>1</sup>, Yoshinari Makimura<sup>1</sup> and Jean-Marie Tarascon<sup>1</sup>; <sup>1</sup>LRCS UMR6007, Amiens, France; <sup>2</sup>LRCS, Amiens, France.

Thanks to a combination of structural, morphological and electrochemical characterizations, the electrochromic mechanism occurring in nickel oxide thin films grown by Pulsed Laser Deposition, was recently proposed [1]. This mechanism is linked to a faradaic process based on the well-known Ni(OH)<sub>2</sub>/NiOOH two-phase system, as a result of a spontaneous chemical conversion of NiO in Ni(OH)<sub>2</sub> at the electrode/electrolyte interface. In addition, the poor durability of the system was attributed to a self-discharge phenomenon associated to a partial dissolution of the oxidized phases. Aiming at limiting the degradation of the electrochromic performances during cycling, or in other words increasing the stability of the oxidized phases, a chemical approach, based on the substitution of nickel for other elements, was used. Ni-M-O (M = Co, Ta, W) thin films were grown, by Pulsed laser Deposition in optimized conditions namely under 10-1 mbar oxygen pressure and at room temperature. Herein, the influence of each additive on the structure, composition, morphology, and the electrochromic behavior of nickel based oxide thin films will be discussed. [1] I. Bouessay, A. Rougier, P. Poizot, J. Moscovici, A. Michalowicz, and J.-M. Tarascon, Electrochim. Acta, Vol. 50(18) 3737 2005.

SESSION E4: Poster Session

Chair: Aline Rougier

Tuesday Evening, November 29, 2005

8:00 PM

Exhibition Hall D (Hynes)

#### E4.1

##### Hydrogen Intercalation Dynamics in Iridium Based Oxides. Jonas Backholm and Gunnar A. Niklasson; Engineering Sciences, Uppsala University, Uppsala, Sweden.

Iridium based oxides are used in electrochromic devices as anodic counter electrodes to the more strongly colouring tungsten oxide. Compared to nickel oxide, the iridium based oxides are less colouring but they show greater chemical stability. To improve the colouration of iridium oxide, and to make it less expensive, additives in form of other metals are added to the oxide forming a mixed electrochromic oxide. Samples of iridium-tantalum-oxide, iridium-tin-oxide, and pure iridium oxide have been prepared onto In<sub>2</sub>O<sub>3</sub>:Sn covered glass substrates with reactive DC magnetron sputtering, using metallic targets. The oxides have then been compared regarding their intercalation processes using galvanostatic intermittent titration technique (GITT), chronopotentiometry, and potentiostatic intermittent titration technique (PITT) using a standard three-electrode setup with the electrochromic film as working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode submerged in propionic acid. In GITT the potential is measured during a short intercalation period and a following, extended, relaxation period, allowing the film to be close to equilibrium during a quasi steady-state measurement. When chronopotentiometry is used the potential is measured while a constant low current is intercalating the film, allowing the film to be analysed away from the equilibrium state. Comparing the result of chronopotentiometry with the result from GITT, it is possible to study the kinetics of the intercalation process. In PITT small potential steps are applied to the film while the charge transfer current is monitored. Both PITT and GITT have proved to be useful methods to determine the solid state diffusion coefficient. If the shape of the electronic bands in the films is assumed to be unchanged by intercalated ions, the chemical potential is believed to follow the Fermi level while the derivative of charge gives the density of states at the Fermi level.

#### E4.2

##### Photolithography of Electrochromic Conducting Polymers.

Arvind Kumar and Gregory A. Sotzing; Department of Chemistry and the Polymer Program, Univ of Connecticut, Storrs, CT 06269-3136, Connecticut.

Here, we present a novel technique to pattern conducting polymers at the micron-scale for large volume applications using a form of conventional photolithography. In this technique a precursor polymer was UV irradiated at 365nm. Then the precursor polymer was developed and converted to conductive polymer. 40 μm conductive

polythiophene lines separated by 60  $\mu\text{m}$  gaps were patterned on glass, Indium Tin Oxide (ITO)-coated glass and ITO-coated poly(ethyleneterephthalate). The patterned polythiophene lines show dark blue color in the oxidized form and yellow color in the neutral form. As the patterned lines are well below the resolution limit of human eyes, this technique can be used to make pixels of differently colored electrochromic materials.

#### **E4.3**

**Enhanced electrochromic properties induced by surface plasmon resonance.** Yoon-Chae Nah, Seok-Soon Kim, Jeong-Ho Park and Dong-Yu Kim; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Surface plasmon resonance (SPR) is an electromagnetic wave occurring when a metal surface is surrounded with a dielectric medium in interaction with incident light. By altering the structure of a metal surface, the properties of SPR can be tailored, which offers the potential for improving electronic and photonic devices. Among all metals, silver show the most intensive SPR absorption in the visible region due to the favorable frequency dependence of the dielectric function. Factors that affect frequency and strength of SPR are size and shape of silver particles, interparticle spacing, and dielectric function of surrounding medium. An electrochemically driven SPR shift could be observed in silver nanoparticles. Electrochromism (EC) is defined as reversible changes in optical absorption under the electrochemical redox reactions. Because of their low power consumption and high coloration efficiency, EC devices have many potential applications such as smart windows, mirrors and displays. There are several reports on which SPR modification occurs at surrounding of EC materials such as tungsten oxide. It has been reported that the absorption shift of metal particles could be induced by change in dielectric function of EC materials during the electrochemical reaction. In our study, we focused on the absorption shift or enhancement of surrounding EC materials induced by silver particles which are synthesized by chemical or electrochemical method on ITO substrate. By controlling the size and distribution of silver particles, we could observe the enhanced absorption of surrounding EC materials.

#### **E4.4**

**WO<sub>3</sub>-Ta<sub>2</sub>O<sub>5</sub> Nanocomposite films for Electrochromic Materials.** Hee-Sang Shim<sup>1</sup>, Hyo-Jin Ahn<sup>1</sup>, Youn-Su Kim<sup>1</sup>, Yung-Eun Sung<sup>2</sup> and Won Bae Kim<sup>1</sup>; <sup>1</sup>MSE, Gwangju Institute of Science & Technology (GIST), Gwangju, South Korea; <sup>2</sup>School of Chemical & Biological Engineering, Seoul National University, Seoul, South Korea.

An electrochromic (EC) material is characterized by its ability to sustain reversible and persistent changes of its optical properties under an applied electric field. In other words, optical change is obtained when an EC material undergoes electrochemical oxidation or reduction under a specific voltage. EC devices, such as displays, smart window, reflectance mirrors, and chemical sensors usually have a battery-like structure. For cathodic EC materials, tungsten oxide films have been extensively studied due to its large optical change, high coloration efficiency and fast response time during double injection and extraction of electrons and cations. However, the chemical stability of this material in the acidic aqueous solution is poor, thus improvement of its chemical stability are required. Recently, stable materials for pHs have been suggested as the passive and protective layer on the electrochromic films such as Ta<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>. In this work, nanocomposite electrodes consisting of tungsten oxide (WO<sub>3</sub>) and tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) have been designed and fabricated using a co-sputtering system with two targets. Effects of their structural and electrochromic properties on electrochemical reaction have been investigated from the X-ray diffraction (XRD) and in-situ transmittance test. Sputtering was conducted in an Ar ambient at a flow rate of 40 SCCM at room temperature. Structural analysis of prepared samples was carried out by transmission electron microscopy (TEM), X-ray diffraction (XRD), and TEM bright field image. To investigate the nature of the nanocomposite electrodes and to evaluate their performance on electrochromic and electrochemical tests were performed using Potentiostat/Galvanostat. The nano-composite films were used as the working electrode, while Pt gauze and Ag/AgCl (sat. KCl) were used as counter and reference electrodes, respectively. The electrolyte was a 0.25 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. Electrochromic properties such as optical modulation with response time were evaluated by in-situ optical measurement system using 633 nm He-Ne Laser during electrochemical reaction. For all nanocomposite films prepared here, the XRD patterns reveal amorphous characteristics. The electrochemical, electrochromic, and microstructural properties of nanocomposite will be described and discussed in detail. References 1. P. J. Gellings and H. J. Bouwmeester, CRC Handbook of Solid State Electrochemistry, ed. C. G. Granqvist (CRC Press, Boca Raton, FL, 1997), Chap. 16, p. 587

2. C. G. Granqvist, Handbook of Inorganic Electrochromic materials (Elsevier, Amsterdam, 1995). 3. K.S. Ahn, Y.C. Nah, Y.E. Sung, Appl. Phys. Lett., 81 (2002) 3930. 4. S. F. Coggan and R. D. Rauh, in: C. M. Lampert and C. G. Granqvist (Ed.), Larger area Chromogenics, SPIE Opt. Engr. Press, Bellingham, 1990, p. 482.

#### **E4.5**

**Pulsed Laser Deposition of Single Crystal Vanadium Dioxide Thin Films on c-Axis Sapphire from a V<sub>2</sub>O<sub>3</sub> Sintered Target.** Jason Kekas and John Muth; ECE Dept, North Carolina State University, Raleigh, North Carolina.

Single crystal thin films of VO<sub>2</sub> on c-axis sapphire substrates were grown by Pulsed Laser beam Deposition (PLD) from sintered polycrystalline V<sub>2</sub>O<sub>3</sub> targets. This is in contrast to the usual method where metallic vanadium targets are used in an oxygen atmosphere, or where thin vanadium metal films are sputtered or evaporated and subsequently annealed in an oxygen environment. The use of sintered V<sub>2</sub>O<sub>3</sub> targets appears to have the advantage of improving the stoichiometry, and reducing the presence of metal droplets. The targets were prepared from V<sub>2</sub>O<sub>3</sub> powder (120 mesh) by pressing under 5000 PSI, and sintering in a nitrogen environment at 650 °C for 9 hours. Sintered targets are then polished until they have a smooth surface. Short pulses from an excimer laser (125mJ) at a rate of 10Hz were used to ablate a V<sub>2</sub>O<sub>3</sub> target, at partial oxygen pressures between 5 and 30 mTorr with substrate temperatures at 700 degrees C. Measurements by X-ray diffraction indicate C-axis oriented films with no secondary phases. Optical transmission measurements and resistivity measurements clearly show a phase transition at 68 °C. Thus, pulsed laser beam deposition (PLD) of VO<sub>2</sub> films from V<sub>2</sub>O<sub>3</sub> targets is shown to be a viable technique for producing high quality VO<sub>2</sub> films.

#### **E4.6**

**Possibility of Electric Field Induced Electrochromism in Highly Oriented LB Films of Phthalocyanine Derivatives and Arachidic Acid.** Hiroshi Yamamoto, Kuori Katayama, Aki Masuda and Nobuyuki Iwata; Electronics and Computer Science, College of Sci. & Technol., Nihon University, Funabashi, Japan.

For flat-panel display applications electrochromic (EC) phenomena have the two serious issues; slow responses and short lives of color changes mainly because of chemical redox reactions. We have proposed a new EC mechanism in which color changes take place by the change of distribution of intra-molecule electrons. We have noticed Aluminum 1, 4, 8, 11, 15, 18, 22, 25, -octabutoxy-29H, 31H-phthalocyanine triethyl siloxide (AlPcTr) which has a large  $\pi$ -electrons' ring and a long side chain. The purposes of this work are to prepare accumulated AlPcTr LB films as the materials model and to investigate the possibility of the electric field induced electrochromism. The LB films were prepared from the mixture solution of AlPcTr and Arachidic acid (AA) which is introduced in order to stabilize the Langmuir film. The chloroform solution of AlPcTr:AA =1:5 was spread on a water subphase of pH = 10.3 which contained 2 mmol/l CaCl<sub>2</sub> and 0.1 mmol /l NaOH. The spread film was accumulated on ITO substrates. We prepared two kinds of LB films. The first type is a simple accumulation of the mixture solution, namely a Y type. The second type is an alternated accumulation of the mixture AlPcTr/AA layer and a pure AA layer, namely a Hetero type. The effect of buffer layers was also studied by the accumulation of 4 layered AA films prior to the LB films. The surface morphology, the accumulated structure was investigated by the AFM image and its line profile. The surface roughness Ra was ca. 1.65nm in the Hetero type films. The surface of the Hetero films was more flat than that of the Y type of films. From consideration of the molecule length of AA, about 2.7nm, it was understood that the accumulation of layer by layer was achieved only in the Hetero type. The optical absorption spectra of the typical two types of LB films were quite different. The absorption peak at ca. 760nm which was attributed from a  $\pi$ - $\pi^*$  transition in the Pc derivative was distinctly broadened in the Hetero film. Its color changed into transparent. As the simulation the absorption spectra of ionized AlPcTr were investigated by a semi-empirical MO calculation. The simulation revealed that definite color changes are resulted in by changing the number of intra-molecule electrons. We thought that the ions included in the LB film with the highly oriented structure do change the distribution of electrons of the AlPcTr molecule. From the comparison with the simulated and experimental results it was thought that the change of the absorption spectra was caused by accompanied anions surrounding AlPcTr molecules. As a conclusion we can expect the possibility of the electric field induced electrochromic color changes.

#### **E4.7**

**Modified thermochromism of VO<sub>2</sub> by Lithium doping.** Bruno Meyer, Angelika Polity, Niklas Volbers and Ganhua Fu; 1. Physikalisches Institut, Giessen, Germany.

Due to the switching of the optical properties at semiconductor-metal phase transition, VO<sub>2</sub> can be used as infra-red light (IR)-switching or bolometric devices or as intelligent energy conserving window coating. For an application as smart window coating, the transition temperature has to be lowered to about 300 K and the transmittance in the visible region should be as high as possible. The former problem can be solved by W doping. Now we try to conquer the latter problem by Li doping. Li doped VO<sub>2</sub> thin films were prepared by rf-sputtering with metallic V and ceramic Li<sub>2</sub>O doped VO<sub>2</sub> targets. The influence of the sputter power, substrate (float glass, ITO and TiO<sub>2</sub> buffer layer) and substrate temperature were investigated. The switching properties are evaluated from wavelength and temperature dependent measurements. Secondary ion mass spectroscopy (SIMS) was used to determine the composition of the films.

#### E4.8

##### **Metal Oxide Nanowires for Electrochromic Sensor**

**Application.** P. K. Jha, K. M. Sawicka and P. I. Gouma; Material Science, State University of NY at Stony Brook, Stony Brook, New York.

Tungsten trioxide and Molybdenum trioxide films were made using sputtering technique and were tested for their gas sensing and electrochromic properties. The WO<sub>3</sub> film showed selective sensitivity towards NO<sub>2</sub> while MoO<sub>3</sub> was selective to NH<sub>3</sub>. The films were characterized using Raman spectroscopy and a shift in spectrum was observed between as sputtered MoO<sub>3</sub> film and gas exposed film indicating protonation of the metal oxide (formation of HXMoOy). Subsequently nanowires of WO<sub>3</sub> and MoO<sub>3</sub> were made by electrospinning technique using metal oxide sol-gel and polymer as precursor, and where found to have better sensing properties than the films obtained by sol-gel and sputtering. These nanowires can be used as gas sensors in which the output signal is the change of color of the sensor.

#### E4.9

**Nickel Oxide Based Thin Films Chemically Deposited for Electrochromic Applications.** Monica Araceli Vidales-Hurtado and Arturo Mendoza; Unidad Queretaro, CINVESTAV-IPN, Queretaro, Queretaro, Mexico.

Nickel oxide based thin films have been obtained by the chemical bath deposition method on different substrates. The precursor solution was a mixture of nickel nitrate, urea and deionized water. The chemistry of the deposition is based on the decomposition of urea at temperatures of 90-100 °C, which promotes the precipitation of Ni(OH)<sub>2</sub> in the solution. X-ray diffraction and infrared absorption data show that as-deposited films is a mixture of the well ordered βII- Ni(OH)<sub>2</sub> and the turbostratic αII- Ni(OH)<sub>2</sub> phases. After thermal annealing in air at temperatures of 300 °C the films are transformed into NiO. The optical constants of as-deposited and annealed films deposited on quartz substrates were obtained from reflectance and transmittance spectra. The refractive index in the visible range is about of 1.61 and 2.2, with an absorption edge of about 4.5 and 3.5 eV for as-deposited and annealed films, respectively. In order to evaluate the electrochromic behavior, nickel hydroxide films were deposited on ITO-coated glass substrates. Cyclic voltammetry was performed on these samples and the optical constants in both states, bleached and colored, were obtained from ex-situ reflectance and transmittance spectra. The dependence of the electrochromic behavior on the composition in solution and annealing temperature is discussed.

#### E4.10

**Cyclic Switching Properties of Polymer Coated Pd/Mg-Ni Switchable Mirrors.** S. Bao, Y. Yamada, M. Okada, P. Jin, M. Tazawa and Y. Yoshimura; Material Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan.

Pd-capped Mg-Ni alloy thin films have received considerable interest as a switchable mirror. Among various materials, Mg-Ni alloy thin films have advantages especially for large window application in the viewpoint of material cost and resource. This material, however, shows rather fast degradation after gasochromic switching using hydrogen containing gas. For example, Pd/Mg<sub>4</sub>Ni thin film does not change after about 150 cycles, which may due to an oxidation of Mg. In this study, we tested the polymer coating of switchable mirror thin film to improve its cyclic durability. The polymer membrane such as polyvinyl acetate (PVAc), polyvinyl chloride (PVC), polystyrene(PS), cellulose acetate (CA), and ethyl cellulose (EC) have an excellent gas separation characteristic that is able to separate the hydrogen and oxygen gas. It is expected that these polymers behave as a prevention membrane to suppress the oxidation of Mg. These polymers with the thickness range between 70 nm to 250 nm are spin coated to the Pd/Mg<sub>4</sub>Ni thin films which are deposited on glass substrate by magnetron sputtering and their cyclic switching properties are

characterized using 4% hydrogen gas in Ar. The cyclic durability of samples coated with a polymer membrane of PVAc, CA, and EC of 100 to 150 nm thickness are about 6 times elongated compared with the non-coated samples. The quantity of the gas that transmit an non-porous membrane is directly proportional to the partial pressure difference of the gas, the transmission area, the transmission time, and inversely proportional to the thickness of the membrane. These results show that the polymer membrane in thickness of 150 nm does not influence the rate of hydrogenation/dehydrogenation so much and is effective to suppress the degradation of the switchable mirrors.

#### E4.11

**Organic Inorganic Hybrid Materials for Electrochromic Device Applications.** David L. Carroll, Manoj A. G. Namboothiry, Kyungkon Kim and Jiwen Liu; Department of Physics, The Center for Nanotechnology and Molecular Materials, Wake Forest University, Winston Salem, North Carolina.

Organic inorganic hybrid electrochromic devices were made using poly(3,4 ethylene dioxathiophene): poly styrene sulfonate(PEDOT:PSS) and nanoparticles of gold, silver and vanadium pentoxide. The effect of plasmonic band of nanoparticles on the electrochromic properties of the hybrid devices were studied. The switching speed is monitored as a function of nanoparticle loading in the hybrid device. The devices were annealed at different temperatures to enhance the electrochromic properties.

#### E4.12

**Vapor Deposition Polymerization and Electrochemical Characterization of Polyimide Thin Films Having Perylene Unit.** Hiroaki Usui<sup>1</sup>, Katsusuke Hibi<sup>1</sup>, Kuniaki Tanaka<sup>1</sup> and Kyoko Kojima<sup>2</sup>; <sup>1</sup>Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan; <sup>2</sup>Central Research Laboratory, Hitachi Ltd., Kokubunji, Tokyo, Japan.

Perylene and its derivatives have attractive characteristics for optical and electronic applications. However, conventionally evaporated thin films have polycrystalline structure that includes morphological and structural imperfections coming from grain boundaries. Moreover, they have limited stability due to the van der Waals nature of the molecules. This paper proposes to prepare uniform and stable polyimide thin films having perylene unit in the main chain. Polyimide thin films were prepared by coevaporation of 3,4,9,10-peryene tetracarboxylic dianhydride (PTCDA) and 1,5-diaminonaphthalene (DAN) or PTCDA and 1,12-diaminododecane (DADD) in high vacuum. The coevaporation produced thin films of polyamic acid, which were imidized by thermal treatment in the air. The films had uniform amorphous structure. The PTCDA-DAN polyimide has higher conductivity and narrower optical bandgap compared to PTCDA monomer film. Electrochemical measurement showed that the polyimide film achieves reversible reduction, and has the possibility of working as n-type semiconductor. The reduction proceeded in two steps, accompanying electrochromism from orange to purple and then to yellowish green at -0.6 V and -1.0 V (vs. Ag/Ag<sup>+</sup>), respectively. PTCDA-DADD polyimide had wider optical bandgap and smaller conductivity compared to the PTCDA-DAN polyimide due to the aliphatic nature of diamine unit. Displacement current measurement for a metal-insulator-semiconductor (MIS) diode indicated that PTCDA-DADD also has the possibility of electron transport. It showed reversible electrochemical reduction accompanying electrochromism from orange to yellowish green. However, the reduction proceeded in one step at -1.0 V with this material. PTCDA monomer film also showed electrochromism, but the polyimide thin films were superior in stability against repeated redox cycles. In conclusion, coevaporation of PTCDA and diamine is a promising method for preparing uniform and stable semiconducting perylene polyimide thin films without using solvent.

#### E4.13

**XAS investigations of WO<sub>3-y</sub> thin films grown by Pulsed Laser Deposition.** Aline Rougier<sup>1</sup>, Jacques Moscovici<sup>2</sup> and Alain Michalowicz<sup>2</sup>; <sup>1</sup>LRCS UMR6007, Amiens, France; <sup>2</sup>LPS2M, Creteil, France.

In spite of substantial research, understanding of the electrochromic mechanism involved in tungsten oxide thin films is still not complete. Aiming at a better understanding of the importance of the oxygen vacancies on the electrochromic properties, tungsten oxide thin films were grown by Pulsed Laser Deposition under a wide range of oxygen pressures (PO<sub>2</sub> < 10<sup>-1</sup> mbar) and substrate temperatures (Ts < 400 °C). Whatever the pressure, X-ray amorphous films were grown for temperatures below 250 °C. For higher substrate temperatures and under 10<sup>-1</sup> mbar oxygen pressure, the broadness of the X-ray peaks and their overlapping lead to difficult phase identification. The structural evolution of the as-deposited films with the deposition conditions as well as on cycling was investigated by X-ray absorption

spectroscopy. The experiments were carried out at LURE, the French synchrotron radiation facility. The data were recorded at the LIII W edge at room temperature and detected by a Total Electron Yield mode. Beneficial comparisons with our earlier work on powders enable us to propose a careful characterization of the WO<sub>3</sub>-y thin films involving the assumption of 3 to 4 different distances for the first coordination shell. Herein, the influence of both the substrate temperatures and the oxygen pressure on the local structure of tungsten trioxide thin films will be discussed.

#### E4.14

**XAS Characterization of Electrochromic Ni-M-O (M = Co, Ta, W) Thin Films.** Aline Rougier<sup>1</sup>, Nicolas Penin<sup>1</sup>, Yoshinari Makimura<sup>1</sup>, Jacques Moscovici<sup>2</sup> and Alain Michalowicz<sup>2</sup>; <sup>1</sup>LRCO UMR6007, Amiens, France; <sup>2</sup>LPS2M, Creteil, France.

Aiming at improving the electrochromic performances of nickel oxide, Ni-M-O (M = Co, Ta, W) thin films were grown by Pulsed Laser Deposition, in optimized conditions namely under 10-1 mbar of oxygen pressure and at room temperature. The determination of the structure of the mixed films (solid solution Ni<sub>1-x</sub>M<sub>x</sub>O<sub>y</sub> or multi-phase system) remains limited by the progressive film amorphisation with increasing M content. On the contrary, X-ray absorption spectroscopy (XAS) was used as a unique tool for the phase identification as well as the understanding of the influence of the additive on the electrochromic mechanism involved in Ni-M-O thin films. The XAS data were recorded at the French and the Italian synchrotron radiation facilities (LURE and ELETTRA) at the Ni K edge (transmission mode and in total electron yields) and at the W LIII edge (in total electron yields and in fluorescence mode). XANES spectra, at the W edge, of PLD-Ni-W-O (5 %t. WO<sub>3</sub>) and PLD-WO<sub>3</sub> thin films, conclude in a similar W6+ oxidation state. On the contrary, the comparison of the EXAFS spectra shows some differences in the distance of the second neighbour shells suggesting that the W environment in the Ni-W-O film is modified from the one in WO<sub>3</sub>. Herein, the evolution of both nickel and M (M = Co, Ta, W) environments and oxidation states vs the M concentration for as-deposited films as well as upon cycling will be discussed.

#### E4.15

**Electrochromic Tungsten Oxide Thin Films Deposited by the Pulsed Pneumatic Spray Pyrolysis Technique: An Electrochemical and Structural Study.** Dwight R. Acosta<sup>1</sup>, Jesus M. Ortega<sup>2</sup>, Arturo I. Martinez<sup>2</sup> and Carlos R. Magana<sup>3</sup>; <sup>1</sup>IFISICA, UNAM, Mexico City, Mexico DF, Mexico; <sup>2</sup>Materia Condensada, IFUNAM, Mexico City, Mexico DF, Mexico; <sup>3</sup>Instituto de Fisica, Universidad Nacional Autonoma de Mexico, Mexico City, Mexico df, Mexico.

Electrochromic thin films of tungsten trioxide were deposited by the pulsed spray pyrolysis technique spraying 20 and 30 mL respectively of 0.2 M solutions of WCl<sub>6</sub> in dimethylformamide at a substrate temperature of 500 Celsius degree on FTO-glass substrate. In this work it has been studied, the substrate effects on the structural properties of the tungsten trioxide layers, e.g. the triclinic structure was obtained when deposited on amorphous glass and on FTP polycrystalline substrates respectively. The tungsten trioxide films deposited on FTO substrate presents differences in their electrochromic behavior which was studied with the cyclic voltammetry technique using as electrolyte, a 0.001M solution of sulfuric acid. Also the effects of FTO substrate on structural, morphological and optical properties of the WO<sub>3</sub> films are presented and discussed. Also we present the results of the synthesis and characterization of tungsten trioxide films when the pulsed spray pyrolysis technique is used in order to produce low cost and large area coatings for several different applications.

#### E4.16

**Fast-Switching, High-Contrast Electrochromic Thin Films Prepared via Layer-by-Layer Assembly.** Jaime C. Grunlan, <sup>1</sup>Mechanical Engineering, Texas A&M University, College Station, Texas; <sup>2</sup>Polymer Technology Center, Texas A&M University, College Station, Texas.

A variety of electrochromic films have been produced recently using the layer-by-layer (LbL) assembly technique. Thin films, typically (< 1μm, are created by alternately exposing a substrate to positively- and negatively-charged molecules or particles in water. Positive and negative depositions are continuously repeated until the desired number of //bilayers// (or cationic-anionic pairs) is achieved. Each individual layer may be 1-100+ nm thick depending on a variety of factors. The ability to control coating thickness down to the nm-level, easily insert variable components without altering the process, and operate under ambient conditions are key advantages of this deposition technique. These thin films often have properties that are comparable to, or enhanced, relative to comparable thick films (>>1μm). Many electrochromic films have been prepared using

intrinsically conductive polymers that exhibit fast switching, but suffer from environmental instability and poor contrast ratio. Higher contrast has been achieved with inorganic oxides, but these films tend to switch states very slowly due to poor electrical conductivity. In an effort to increase the switching speed of LbL electrochromic films, without sacrificing contrast ratio, a three-component system was prepared. In this case, high-contrast tungstate anions (WO<sub>4</sub><sup>2-</sup>) were alternated with poly(4-vinylpyridine-co-styrene) (PVP-S) and PDDA-stabilized indium tin oxide (ITO) nanoparticles to create a four-layer repeating structure (i.e., PVP-S and PDDA-ITO were each deposited every fourth layer). In the absence of the PDDA-ITO particles, this system exhibits a contrast ratio > 8 (equivalent to newspaper print) with 60-bilayers, but the time taken to switch states is 25 seconds. Unlike tungstate, ITO has a high intrinsic conductivity (~ 10<sup>4</sup> S/cm) that reduces the switching speed to 3 seconds without altering the contrast ratio. It is only with the control afforded by the ESA process that switching speed and contrast ratio can be optimized simultaneously. Further improvements could be achieved by negatively stabilizing the ITO in an effort to deposit from the same solution as the tungstate anions, which would reduce the number of layers required to achieve the same properties.

#### E4.17

**Electrochromic Properties of Obliquely Sputtered Indium Nitride Films.** Jun-ichi Yamazaki<sup>1</sup>, Toshihide Kuranaga<sup>1</sup>, Yasushi Inoue<sup>2</sup>, Nagahiro Saito<sup>1</sup> and Osamu Takai<sup>2</sup>; <sup>1</sup>Graduate School of Eng., Nagoya Univ., Nagoya, Japan; <sup>2</sup>EcoTopia Science Inst., Nagoya Univ., Nagoya, Japan.

Electrochromic (EC) materials have a unique optical property to reversibly change their colors with applying an electrical potential in a solution. Indium nitride (InN) has one of the few nitrides that show electrochromism, and their EC mechanism may be different from that of other inorganic EC materials. We have proposed that the color change in InN is ascribable to so-called Burstein-Moss shift of the optical absorption edge induced by an alternate adsorption of H<sup>+</sup> and OH<sup>-</sup> on the InN surface. Based on this hypothesis, the EC properties of InN films can be improved by modifying film structure to widen effective surface defined as the interface between InN solid state and the solution. In this study, we prepared nano-structured InN films by means of oblique-angle sputter deposition in order to improve the EC properties of the InN films. InN films were prepared by a rf (13.56 MHz) magnetron sputtering equipment. The rf power was kept at 75 W with an N<sub>2</sub> pressure of 1 Pa throughout the deposition process. The angle  $\theta$  of a substrate holder against the incident flux of In was varied in order to deposit films utilizing shadowing effect. The substrate rotation speed was set to 10 rpm. The structure of the films was characterized by XRD, XPS, and SEM. The EC properties of the InN films in Na<sub>2</sub>SO<sub>4</sub> aqueous solution were investigated by using a double-beam optical spectrometer. XRD analysis proved that the InN films exhibit a wurtzite structure with strong 001 preferred orientation independent of the substrate angle  $\theta$ . SEM observation clearly showed the oblique-deposited InN films have nano-size gaps among columnar crystal grains compared to the normally-deposited InN films. The absorption coefficient difference for the oblique deposited films between at an anodic state (+1.0V vs. SCE) and a cathodic state (-1.0V vs. SCE) were 7.3 8.0 times larger than that of films deposited at  $\theta=0^\circ$ . Using oblique sputter deposition, the reaction site in the InN films are extended, and the color change has made improvement due to increasing the amount of H<sup>+</sup> and OH<sup>-</sup> adsorption on the InN surface. Density measurement revealed the packing factor decreases with increase in the angle  $\theta$ , which means the shadowing effect is more efficient at higher  $\theta$ . However, there is no apparent  $\theta$ -dependence of the color change for the oblique-deposited films. It is considered that the effective surface area of the oblique-deposited films does not expand drastically in higher region of the deposition angle  $\theta$ , since the number of the column for each unit area decreases though the gaps in the InN thin films are widened due to the shadowing effect. The surface area of the films estimated from film morphology was actually similar to each other, 5.0 6.4 times larger than the films deposited at  $\theta=0^\circ$ .

#### E4.18

**Influence of volume changes in the thermodynamics of Li intercalation into amorphous WO<sub>3</sub>.** Jorge Garcia Canadas<sup>1</sup>, Germa Garcia-Belmonte<sup>1</sup>, Juan Bisquert<sup>1</sup> and Carles Person<sup>2</sup>; <sup>1</sup>Departament de Ciències Experimentals, Universitat Jaume I, Castellon de la Plana, Castellon, Spain; <sup>2</sup>Departament de Fisica Aplicada i Optica, Universitat de Barcelona, Barcelona, Barcelona, Spain.

Amorphous intercalation materials are useful as electroactive electrodes for lithium batteries, supercapacitors and electrochromic windows. Amorphous films often display a monotonic variation of the electrode potential with the insertion level  $x=n/N$ , (where n and N are the number densities of inserted ions and host atoms, respectively). Usually in amorphous films, cell voltage change has



been interpreted considering distributions of site energies for intercalant species [1]. Recently, we have proposed [2-4] an alternative explanation by regarding contributions to the chemical potential of  $\text{Li}^+$  inside the amorphous film caused by host distortions induced during intercalation. In this approach the chemical potential takes the form [3]  $\mu(x) = E_0 + (1+\eta)Gx^\eta + Ux + \beta^{-1} \ln(x/(1-x))$  (1) In this equation the first term  $E_0$  corresponds to a constant energy level, the second one  $(1+\eta)Gx^\eta$ , being  $G$  and  $\eta$  parameters, relates to the dependence of the intercalant-host interaction with the insertion level. The term  $Ux$  represents the interparticle interaction contribution, and the last summand includes the entropic term ( $\beta^{-1} = k_B T$  is the thermal energy). This approach highlights contributions to the chemical potential arising from volume changes, caused by the intercalation process itself. Better accommodation of strain induced by lithium insertion/removal is believed to improve electrode cyclability. Volume changes have then an influence on the cell voltage. This fact has already been considered by Vakarin et al. [5], that proposed an expression for the chemical potential taking into account the linear elasticity theory, involving the concentration dependent stress and strain fields, that accounts for the volume dilatation in the host due to intercalation,  $\mu(x) = \mu_0(x) + S(x)d\epsilon(x)/dx - (d\sigma(x)/dx)\epsilon(x)$  (2) Where,  $\mu_0(x) = E_0 + Ux + \beta^{-1} \ln(x/(1-x))$ , (3) and  $S(x)$  is the actual stress, defined as  $S(x) = -\lambda d\mu/dx - \epsilon(x) - \sigma(x)$  (4) Being  $-\lambda d\mu/dx$  an elastic constant,  $\epsilon(x)$  the strain produced by the intercalation and  $\sigma(x)$  the force (stress) applied by the guest. The purpose of our contribution is to relate our model (Eq. 1) with that proposed previously (Eq. 2). To do that we have measured experimentally the elastic constant  $-\lambda d\mu/dx$  and the relative volume changes of a set of a- $\text{WO}_3$  films with different thicknesses. By relating our model (Eq. 1) with Eq. 2 and introducing these experimental data, we obtain as a result that host-guest interaction parameter  $G$  informs on the volume expansion undergone by the host lattice during intercalation. References [1] M. Stromme, Phys. Rev. B 58 (1998) 11015. [2] G. Garcia-Belmonte, V.S. Vikhrenko, J. Garcia-Canadas, J. Bisquert, Solid State Ionics 170 (2004) 123. [3] J. Garcia-Canadas, G. Garcia-Belmonte, J. Bisquert, I. Porqueras, C. Person, Solid State Ionics (2005) In Press. [4] J. Garcia-Canadas, F. Fabregat-Santiago, I. Porqueras, C. Person, J. Bisquert, G. Garcia-Belmonte, Solid State Ionics 175 (2004) 521. [5] E. V. Vakarin, J. P. Badiali, Solid State Ionics 171 (2004) 261.

SESSION E5: Polymers for Electrochromics II  
Chair: Aline Rougier  
Wednesday Morning, November 30, 2005  
Room 305 (Hynes)

#### 8:30 AM \*E5.1

**Variable Band Gap Conjugated Polymers for Hybrid Electrochromic Devices.** John R. Reynolds<sup>1</sup>, Aubrey L. Dyer<sup>1</sup>, Avni Argun<sup>1</sup> and Roger J. Mortimer<sup>2,1</sup>; <sup>1</sup>Chemistry, Univ. of Florida, Gainesville, Florida; <sup>2</sup>Chemistry, Loughborough University, Loughborough, United Kingdom.

By controlling the electron-rich character and degree of pi-overlap along a conjugated polymer chain, a family of multi-colored electrochromic (EC) polymers has been developed. Within this, low band gap polymers provide cathodically coloring materials, while high band gap polymers provide anodically coloring materials. A broad spectral variation is accomplished via copolymer composition yielding films whose colors range through yellow-orange-red-purple-blue. Polymers with two transitions in the visible region absorbing red and blue light appear green. When complementary anodically and cathodically coloring polymer pairs are utilized in absorption-transmission configured EC devices, large changes in visible light transmission can be rapidly modulated (sub-second switching). These EC polymers can be matched with molecular electrochromes, such as the cathodically coloring viologens, and the solid state electrochromes, such as the anodically coloring Prussian blue, to provide hybrid devices with the combined optical response of each EC material. Patterning of electronic devices is essential for fabrication of independently addressed displays with high resolution values. Line patterning, which involves printing of patterns on a plastic or paper substrate using a commercial printer, has been utilized for preferential deposition of transparent poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT/PSS) or electrodeless gold films with lateral resolution values of approximately 30 microns. These electrodes were used to build laterally configured polymer and metallic interdigitated electrodes (IDEs) for electrochromic devices (ECDs). We have introduced the use of highly porous metallized membranes in patterned reflective ECDs which allows fast EC switching of dioxothiophene based polymers (5 to 10 Hz) with outstanding power efficiencies and long-term stabilities. Using metallized porous electrodes, reflectance attenuation of up to 90% in the NIR and 60% in the visible regions are obtained. These display devices operate at low voltages (+1 V)

and have low energy requirements to switch. We have developed a method to electrically contact patterned electrodes on porous substrates where the contacts are hidden on the back of the substrates. This method permits increased density and more design flexibility for display type devices as compared to conventional front-side contact techniques. A numeric display ECD was designed and assembled to demonstrate the independent addressing of patterned electrodes with back-side contacts.

#### 9:00 AM E5.2

**Synthesis of functionalized conjugated polymers for thin film coating applications.** Sze C. Yang, Wenguang Li, Zhexiong Tang and Ping Ren; Chemistry, University of Rhode Island, Kingston, Rhode Island.

Polyaniline, polythiophene and polypyrrole have been shown to exhibit reversible electrochromic property. These conjugated polymers have been considered as coatings for smart window applications. Being a polymeric material, it has the potential for large-area, flexible electrochromic devices. Electrochemical deposition of conjugated polymer is the common method for coating small area electrochromic devices. For large-area electrochromic devices, electrodeposition is not a practical manufacturing process. The high cost, and the difficulty for producing a uniform electrochromic film are the problems. It is desirable to synthesize conjugated polymers that are soluble in water or organic solvents for large-area coating applications. In this paper, we present a synthetic method for functionalizing conjugated polymers that are convenient for coating of large-area electrochromic devices. The functionalized polymer has the structure of a double-strand polymer. It is a non-covalently bonded molecular complex between two linear polymers. The first strand is the electrochromic polymer; and the second strand is a polymeric dopant. The second strand serves the functions of charge balance (as a dopant to maintain conductivity), chemical stabilization, and processibility. Using a double-strand approach, we avoided direct chemical substitution at the conducting polymer backbone, and minimized the disruption of the electronic conjugation of the conducting polymer. The second strand in the complex provides the properties needed for the coating process without compromising the electrochromic properties of the conjugated polymer.

#### 9:15 AM E5.3

**Smart Windows Based on Electrochromic Polymers.** Chunye Xu, Lu Liu, Dai Ning, Calen Kaneko, Fengyu Su and Minoru Taya; University of Washington, Seattle, Washington.

In the next twenty years, several percent of all energy used in the United States will be consumed by residential windows. As a result of these findings, research into reducing waste heat in residential and commercial buildings has become an important field. A promising technology, developed to face this challenge, is electrochromic or smart, switchable windows. These windows are capable of controlling the throughput of radiant energy, potentially greatly reducing the amount of electricity consumed by heating and air conditioning by allowing sun in during the winter and blocking it during the summer. Smart windows are categorized by trigger into three main areas, thermotropics, photochromics and electrochromics. Here is introduced a fast response and energy efficient electrochromic window. Electrochromic windows are composed of five layers, a conductive transparent, an electrochromic active, an ion conductive, an ion storage and a second conductive transparent layer. Conjugated polymer, Poly[3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine] (PProDOT-Me2), was used as a blue electrochromic active layer and inorganic vanadium pentoxide film was utilized as an ion storage layer. Two assembly methods were described corresponding to two types of electrolyte, gel and liquid electrolytes. Dimension of smart window up to 12 x 20 inch was developed. UV curable sealant was applied for the sealing devices. Color changing or switching speed of 12 x 20 inch smart window is less than 15 seconds under applied 1.5-2.0 voltage. Red and green color electrochromic polymers were developed lately and will be demonstrated. Multicolor, high contrast ratio, fast switching speed, long open circuit memory and lifetime are our study goals. Additional applications of the smart window were discussed as well.

#### 9:30 AM E5.4

**All-Organic Active Matrix Addressed Displays Based on Electrochromic Polymers and Flexible Substrates.** Peter Andersson<sup>1</sup>, Payman Tehrani<sup>1</sup>, Robert Forchheimer<sup>2</sup>, David Nilsson<sup>1</sup>, Nathaniel Robinson<sup>1</sup> and Magnus Berggren<sup>1</sup>; <sup>1</sup>Dept. of Science and Technology, Linköping University, Norrköping, Sweden; <sup>2</sup>Dept. of Electrical Engineering, Linköping University, Linköping, Sweden.

Here we present actively addressed matrix displays based on all-organic smart pixels controlled by electrochemical switching. This

work is a continuation from previous results presented by Andersson et al. in *Advanced Materials*, Vol. 14, pp. 1460-1464 (2002). The smart pixel, included in each intersection of a cross-point matrix, is an electrochemical transistor in conjunction with an electrochromic display cell. Each transistor and display cell consists of a patterned solidified electrolyte sandwiched between patterned PEDOT:PSS (poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate)) electrodes, where the electronic and optical properties of PEDOT:PSS are used in the transistor and the display cell, respectively. The novelty of this work lies in the utilization of a vertically designed three-terminal electrochemical transistor that eliminates the need for over-lapping conducting PEDOT:PSS address lines in the matrix display. Thus, the three-terminal transistor allows for simplified manufacturing that can be performed in fewer steps. The bi-stability of the electrochromic cells together with the on/off-ratio of the transistors reduce the power consumption and cross-talk in the matrix display. Improving the contrast of the display by combining PEDOT:PSS with other electrochromic polymers, and improving the display cell fill-factor will also be discussed.

#### 9:45 AM E5.5

**Organic Electrochromic Materials for Color Paper-Display.**  
Norihisa Kobayashi<sup>1,2</sup>, Mami Nishimura<sup>2</sup>, Shohei Miura<sup>2</sup> and Yutaka Goh<sup>3</sup>, <sup>1</sup>Dept. Information & Image Sci., Chiba University, Chiba, Japan; <sup>2</sup>Graduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan; <sup>3</sup>Japan Chemical Innovation Institute, Chiba 263-8522, Japan.

We studied organic electrochromic materials, which showed reversible color change by electronic stimuli, from a view point of paper-like electronic imaging device. Electrochemical and spectroscopic measurements with cyclic voltammogram, chronoamperometry and in situ spectrometry were carried out for a series of phthalate derivatives, which showed vivid color change to cyan, magenta or yellow upon electrochemical stimulation, to clarify its electrochromic behaviors. Further, passive-matrix operation of a three-layered (cyan, magenta and yellow) electrochromic display has also been demonstrated.

SESSION E6: Inorganic/Organic Electrochromics I  
Wednesday Morning, November 30, 2005  
Room 305 (Hynes)

#### 10:30 AM \*E6.1

**Adjustable Reflectivity Smart Window.** D. Morgan Tench, M. A. Cunningham, J. J. Kuo and L. F. Warren; Rockwell Scientific Company, Thousand Oaks, California.

The current state of development of a reversible electrochemical mirror (REM) device for smart window applications will be described. The device comprises a gelled gamma-butyrolactone (GBL) electrolyte sandwiched between a mirror electrode and a dot matrix counter electrode. The mirror electrode is indium tin oxide (ITO) with a thin overlayer of sputtered platinum (15Å), which acts as a nucleation layer so that highly-reflective electrodeposits are obtained. The dot matrix electrode comprises platinum nuclei distributed on an ITO layer, which acts as a transparent current collector. Light reflectance is increased by electrodeposition of silver metal on the mirror electrode, and device transmission is increased by electrodeposition of silver on the dot matrix counter electrode. Light reflectance can be continuously varied over a wide range, providing high efficiency for controlling heat flow in buildings and transportation vehicles. No voltage is required to maintain a given mirror state. Key technical challenges to commercialization of the REM smart window have included attaining uniform switching over large areas and inexpensive fabrication of the dot matrix electrode. Switching uniformity can be improved by use of a resistive innerlayer of transparent material in the counter electrode to overshadow or offset the counter electrode sheet resistance. Inexpensive dot matrix electrode fabrication was attained by electrodepositing the platinum nuclei at inherent active sites on the ITO surface. Electrodeposition from a commercial Pt plating bath consistently provides the optimum dot density for the counter electrode (1 - 3 million/cm<sup>2</sup>) without the use of photolithography.

#### 11:00 AM E6.2

**New Concepts for the Realisation of Flexible Materials with Tuneable Emissivity.** Mathieu Morcrette<sup>1</sup>, Lionel Beluze<sup>1,2</sup>, Bruno Viana<sup>2</sup>, Jean-Claude Badot<sup>2</sup> and Jean-Marie Tarascon<sup>1</sup>; <sup>1</sup>Laboratoire de Reactivite et de Chimie des Solides, Amiens, France; <sup>2</sup>Laboratoire de Chimie Appliquee de l'Etat Solide, Paris, France.

There is more and more interest in the control of emissivity or reflectivity for various applications such as, for instance, smart windows or thermal control of satellites. All these applications require the control of the IR radiation either emitted or reflected by the system, which can be done by fitting an IR emissivity/reflectivity

modulator layer on the surface of the system considered. We have recently developed such a device that lies in the use of powder material embedded in a plastic matrix according to the so-called PLiON technology. The use of materials in divided state enables us to build a light and flexible device that can fit various shapes and can enable to build large size devices. However, using powders triggers new issues like the consequence of the scattering phenomenon on the optical properties of the films. An average 42 % reflectance contrast in the 4 - 16 μm spectral range was found for optimized WO<sub>3</sub>.H<sub>2</sub>O powders that combine high reflectivity/emissivity contrast in the infrared spectral range, good electrochromic efficiency and electrochemical reversibility. While presently satisfying, the main drawback of this device is the kinetic of the switching time that can be improved by a careful control of the thickness of the different layers of the device but with penalties in the contrast of the device. In the first part of this presentation, we will present a screening of different materials together with a simple model that was helpful to understand their optical behaviour. We will see that IR modulation can be obtained both with low or highly absorptive materials. We will end this part by a discussion aimed towards drawing a strategy to choose good IR modulator materials. In the second part, we will present rapidly modified / alternative devices to the PLiON technology that allows a certain increase of the kinetics thanks to the modification of the polymer composition and/or the use of the electrodeposition technique as the active process for IR modulation. We will present the advantages and drawbacks of these two modifications in the properties of devices (switching time, contrast,...).

#### 11:15 AM E6.3

**XPS, UPS and SXPS analysis of V2O5 films deposited by RF sputtering and Atomic Layer Deposition.**

Massimiliano Liberatore<sup>1</sup>, Andreas Thissen<sup>1</sup>, Wolfram Jaegermann<sup>1</sup>, Frederique Donsanti<sup>2</sup>, Konstantina Kostourou<sup>2</sup> and Franco Decker<sup>2</sup>; <sup>1</sup>Material Science, Technical University of Darmstadt (TUD), Darmstadt, Germany; <sup>2</sup>Chemistry, University of Rome "La Sapienza", Rome, Italy.

In the last decade a large amount of studies have demonstrated that vanadium pentoxide thin films are materials useful for construction of technological devices as lithium microbatteries and electrochromic windows. In this scientific survey, we have produced vanadium pentoxide thin films using two different methods: RF sputtering and atomic layer deposition (ALD); we have chosen several substrates such as aluminium and glass coated with chromium or fluorine doped tin oxide (FTO). The films were studied immediately after deposition and after one or more electrochemical insertion/de-insertion cycles. For the photoemission spectroscopy, we have used both conventional (XPS, UPS) and synchrotron light (SXPS) sources. Before electrochemical treatment, all the samples analysed, have show a surface composition of vanadium pentoxide with a small percentage of vanadium in +4 oxidation state. Moreover, the spectra reveal peaks relevant to the presence of sodium and silicon. This features are due to the migration of elements from the substrate to the surface, during the annealing step. An experimental set - up consisting of an electrochemical cell directly connected to the vacuum chamber - allows sample analysis avoiding air contamination after electrochemical treatment. We have investigated both the valence band emissions and the core level lines of vanadium, oxygen, lithium and other elements presented on the surface. Independently from the deposition method, the intercalated samples show a Fermi level shift to higher energies. Core level spectra indicate the reduction of vanadium to oxidation state +4 in concomitance with the growing of a peak relevant to the 1s lithium orbital. Thanks to the synchrotron light, by increasing the intensity of the 1s lithium line we managed to study precisely the lithium behaviour. Therefore, upon prolonged electrochemical cycling, the signals relevant to chlorine and carbon of carbonate anion rise up. These signals are related to the adsorption and decomposition of the electrolyte, respectively. On those samples, it is also in course a comparative study on the effect of vapour phase and electrochemical intercalation .

#### 11:30 AM E6.4

**Li and Na intercalation in V2O5: electrochemical study and study of surface of thin films produced by ALD.**

Frederique Donsanti<sup>1</sup>, Konstantina Kostourou<sup>1</sup>, Franco Decker<sup>1</sup>, Massimiliano Liberatore<sup>2</sup>, Andreas Thissen<sup>2</sup> and Wolfram Jaegermann<sup>2</sup>; <sup>1</sup>Chemistry, Universite Studi di Roma La Sapienza, Roma, Italy; <sup>2</sup>Material science, Technical University of Darmstadt, Darmstadt, Germany.

Thin films of vanadium pentoxide are widely used for ion insertion materials, especially for Li batteries and electrochromic windows. We have made alkali ion (Li+, Na+) intercalation into thin films of V2O5 produced by Atomic Layer Deposition (ALD). The ALD process is a chemical vapour deposition technique where the precursors are injected in the preparation chamber alternatively. With this technique, films with a good homogeneity, uniform for large surfaces

and a thickness below 100 nm were obtained. We deposited V2O5 on two types of conducting substrates, FTO-glass and Cr-glass. Firstly, we studied the structure of the film which is amorphous after deposition and crystalline after an appropriate annealing at 450 °C, and its optical properties (refraction index, band gap.). In a second step, we performed electrochemical intercalation of Li or Na into the films via slow cyclic voltammetries (SSCV) in the safe range from 2.0 to 3.7 V for Li and Na. We performed EIS experiments and PITT experiments as well. In the SSCV experiments on Li: V2O5 four peaks appeared, two anodic and two cathodic, which demonstrate that the intercalation of the alkali ions is almost reversible. From EIS experiments, we can conclude that in the low-frequency domain there is a capacitive behavior and at medium and high frequencies there is a solid-state diffusion of Li (Na) ion into the V2O5 films deposited on FTO substrate. From PITT experiments, we found that the diffusion coefficient changes with the crystal phase of the film, which is changing with the quantity of cations introduced. From XPS experiments, we demonstrated that the oxidation state of vanadium changed with intercalation from 5+ to 4+ and the formation of Li carbonate and Li oxides. We also studied the variation of the optical parameters of V2O5 with the introduction of the ions in the film. The band gap increased with the increase of cations in the films and the colour of the film changed too. V2O5 which is initially yellow, became green after introduction of 1 mol of Li (LiV2O5) in the film. This phenomenon is reversible. We studied also the variation of the refractive index, *n*. All such results have been confirmed with the UPS experiments, which demonstrated that the Fermi level increased with the alkali ion intercalation and that the band gap increased as well. A study of the correlation of the Auger parameter and the optical parameters is in progress.

#### 11:45 AM E6.5

**Enhanced Electro-Chromism in DC Magnetron Sputtered Titanium Oxy Nitride Thin Films: A Report.**  
Karupphasamy Aasai and Aryasomayajula Subrahmanyam; Physics, Indian Institute of Technology, Chennai, Tamil nadu, India.

Electro-chromism has been exhibited in the oxides of tungsten, molybdenum and titanium. In the present investigation, an enhanced electrochromic behavior in Titanium oxynitride ( $\text{TiO}_x\text{N}_y$ ) thin films prepared by pulsed DC Magnetron sputtering technique (in the constant current mode: 0.3 amperes) is reported. These  $\text{TiO}_x\text{N}_y$  thin films have been prepared on glass, quartz and single crystal silicon substrates at a temperature of 420 °C. The target is a pure titanium metal sheet. The reactive gas (nitrogen) flow rate is controlled such that the chamber pressure changes systematically in the range  $7 \times 10^{-4}$  to  $2 \times 10^{-3}$  mbar; the sputter gas (oxygen) flow rate is kept constant such that the chamber pressure remains at  $2.5 \times 10^{-2}$  mbar. The  $\text{TiO}_x\text{N}_y$  thin films have been studied for the crystal structure and surface morphology. The crystallinity / grain size of the films was found to increase with increase in the nitrogen partial pressure. The spectrophotometric data show that the coloration intensity (transmission at 633 nm) in these thin films changes from 89 % to 7.0 %. The Contact potential difference / work function of these  $\text{TiO}_x\text{N}_y$  thin films were measured using a Kelvin probe technique and attempts have been made to quantify the charges responsible for coloration. The cyclic voltammetry technique using a potentiostat with a standard three-electrode configuration consisting of the sample as the working electrode was employed to characterize the electrochromic behavior of these films (1 M  $\text{LiClO}_4$  in propylene carbonate and  $\text{H}_2\text{SO}_4$  were used as electrolytes). The optical modulation and the coloration efficiency for these films with a nitrogen pressure of  $8.4 \times 10^{-4}$  mbar are 82 % (at 633 nm) and  $35 \text{ cm}^2/\text{Coul}$  respectively.

SESSION E7: Inorganic/Organic Electrochromics II  
Chair: Franco Decker  
Wednesday Afternoon, November 30, 2005  
Room 305 (Hynes)

#### 1:30 PM E7.1

**Structural and Spectroelectrochemical Characterization of  $\text{CeVO}_4$  Films Prepared Using a Peroxo Synthesis Route.**  
Angela Surca Vuk, Boris Orel, Robi Jese and Ivo Jerman; Laboratory for Spectroscopy of Materials, National Institute of Chemistry, Ljubljana, Slovenia.

Stoichiometric ceria-vanadia oxides have been investigated in the past from the point of view of their possible application in the fields of catalysis and luminescent materials. In addition, due to their high charge capacity, they have also been used in various iono-optic devices, e.g., as counter electrodes in electrochromic cells. Various synthesis routes have been used for the preparation of powders and films, the former mostly being prepared using solid-state reactions between pure oxides, oxidation of  $\text{CeVO}_3$  in air, wet chemical

synthesis and microwave irradiation, with the films being made by deposition from sols (sol-gel), electrolysis and reactive radio frequency sputtering. Herein, we report the preparation of  $\text{CeVO}_4$  films using a modified peroxo synthesis route which was reported for first time by Kudo [1] and has already been used for the preparation of other intercalation films like  $\text{SnO}_2$  [2],  $\text{WO}_3$  [3],  $\text{Li}_x\text{CoO}_2$  and  $\text{Li}_x\text{NiO}_2$  [4]. The  $\text{CeVO}_4$  films were prepared from vanadium (V) oxoisopropoxide and  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  precursors with the use of  $\text{H}_2\text{O}_2$ . The films were deposited from these sols by dip-coating and heat-treatment at 400 and 500 °C. X-ray diffraction showed that the tetragonal crystalline structure of the mineral Wakefieldite developed with a grain size of 15-20 nm (500 °C, 1h). The UV-visible absorption spectroelectrochemical response of the films was tested in 1M  $\text{LiClO}_4$ /propylene carbonate electrolyte. The results revealed an optical modulation below 5 %T and charge densities between -12 and -20  $\text{mC cm}^{-2}$ , depending on preparation conditions and film thickness (40-60 nm). Using cyclic voltammetry it was possible to observe the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  and  $\text{V}^{5+}/\text{V}^{4+}$  redox changes in the films. Transmission infrared (IR) measurements confirmed the formation of  $\text{CeVO}_4$  with the appearance of two  $\nu_3$  TO modes:  $E_u$  mode as a sharp band at  $768 \text{ cm}^{-1}$  and  $A_{2u}$  as a shoulder band at  $840 \text{ cm}^{-1}$ . The weak band at  $444 \text{ cm}^{-1}$  is a  $\nu_4$  ( $E_u + A_{2u}$ ) deformational mode. In contrast, Near Grazing Incidence Angle (NGIA) spectra (LO modes) revealed only one strong band at  $912 \text{ cm}^{-1}$  which corresponded to the  $E_u$  lattice mode of the crystalline  $\text{CeVO}_4$ . The LO stretching mode of Ce-O at  $580 \text{ cm}^{-1}$ , usually found in crystalline  $\text{CeO}_2$ , was not detected, corroborating the existence of  $\text{CeVO}_4$  and the presence of  $\text{Ce}^{3+}$ . The results of ex-situ transmission and in-situ NGIA IR measurements were compared with those of an in-situ ATR IR spectroelectrochemical cell, recently constructed in our laboratory. The results confirmed the advantages of the new peroxo synthesis route. [1] T. Kudo, Nature 312 (1984) 537. [2] U. Opara Krašovec, B. Orel, S. Hočvar, I. Mušević, J. Electrochem. Soc. 144 (1997) 3398. [3] U. Opara Krašovec, A. —\*ucarons\*—urca Vuk, B. Orel, Electrochim. Acta 46 (2001) 1921. [4] F. —\*ucarons\*—vegl, B. Orel, V. Kaučič, Solar Energy 68 (2000) 523.

#### 1:45 PM E7.2

**Electrochromic WO3 Nanoparticles Consisting of Nanorods and Nanospheroids.** Rohit Deshpande<sup>1,2</sup>, Se-Hee Lee<sup>1</sup>, Philip Parilla<sup>1</sup>, Harv Mahan<sup>1</sup>, Kim Jones<sup>1</sup>, Bobby To<sup>1</sup>, Saibal Mitra<sup>2</sup> and Anne Dillon<sup>1</sup>; <sup>1</sup>National Renewable Energy Laboratories, Golden, Colorado; <sup>2</sup>University of Tulsa, Tulsa, Oklahoma.

Tungsten oxide ( $\text{WO}_3$ ) films hold great promise for a variety of applications including electrochromic windows, gas and humidity sensors, optical devices, photo-catalysis, and high energy density batteries. Films made out of nanostructured tungsten oxide materials should enhance the overall performance in any of the aforementioned applications. Designing nanostructures (where the shortest dimension represents the diffusion path) while maintaining the right crystalline structure may be key to a material with fast insertion kinetics and superior overall device performance. We have recently reported a simple hot-wire chemical vapor deposition technique for the gas-phase synthesis of crystalline tungsten oxide nano-rods and spheroids. Here we report on the electrochromic properties of crystalline nanoparticle  $\text{WO}_3$  thin films. The nanoparticle films are prepared using a novel technique. Electrochromic and optical properties of the films are compared to conventional amorphous and crystalline tungsten oxide films synthesized using evaporation and RF-sputtering techniques, respectively. Electrochromic measurements are performed in an electrochemical cell composed of the tungsten oxide film as the working electrode, platinum foil as the counter electrode, and  $\text{Ag}/\text{AgCl}$  as the reference electrode. Compared to amorphous  $\text{WO}_3$  films, the  $\text{WO}_3$  nanoparticle films show greater current density for proton intercalation. The electrochemical functional improvement is attributed to the larger active surface area of the nanometer-scale  $\text{WO}_3$  particles. Optical measurements indicate high coloration efficiency values of ( $\sim 50 \text{ cm}^2/\text{C}$ ) comparable to the state-of-the-art amorphous films and significantly better than crystalline films. Transmission electron microscopy analyses show that the nanoparticles consist of predominantly nanorods and nanospheroids with diameters between 10-20 nm. X-ray diffraction and Raman spectroscopy are employed to reveal the crystalline structure of the nanoparticles. (1) Mahan, A. H.; Parilla, P. A.; Jones, K. M.; Dillon, A. C. Chem. Phys. Lett. (in press).

#### 2:00 PM E7.3

**Electrochemical Polymerization of Aniline on Self-Assembled Monolayer Modified ITO Electrodes.** Rodolfo Cruz-Silva, Maria E. Nicho and Mary C. Resendiz; Laboratorio de Polimeros, Centro de Investigacion en Ingenieria y Ciencias Aplicadas, Cuernavaca, Morelos, Mexico.

Surface modified ITO electrodes are being studied due to its potential application in organic light-emitting diodes. In this work, polyaniline thin films were deposited by cyclic voltammetry on ITO electrodes

modified by a self-assembled monolayer of N-phenyl- $\gamma$ -aminopropyl-trimethoxysilane (PAPTS). The surface modification of ITO electrodes was confirmed by AFM phase-contrast images and contact-angle measurements. Electrochemical oxidation of the PAPTS monolayer by cyclic voltammetry in aniline-free aqueous electrolyte displays the typical shape of a surface-confined monomer, due to the aniline moieties of the monolayer. An increase in the initial oxidation rate was observed for the PAPTS modified ITO electrodes although the overall film formation rate was slower compared to unmodified ITO electrodes. Morphology changes in the polyaniline film are observed in AFM topographic images, indicating that smoother films are grown in the PAPTS modified ITO compared to films grown on unmodified ITO. The role of the PAPTS monolayer as adhesion promoter for electrochemically deposited polyaniline films on ITO is also discussed.

2:15 PM [E7.4](#)

Abstract Withdrawn

3:30 PM [E7.5](#)

**Growth of Tungsten Oxide Nanorods in Hot Filament Chemical Vapor Deposition.** [Karthikk Sridharan](#)<sup>1</sup>, Rohit Deshpande<sup>1,4</sup>, Kenneth Roberts<sup>2</sup> and Saibal Mitra<sup>3</sup>; <sup>1</sup>Chemical Engineering, University of Tulsa, Tulsa, Oklahoma; <sup>2</sup>Chemistry and Biochemistry, University of Tulsa, Tulsa, Oklahoma; <sup>3</sup>Physics and Engineering Physics, University of Tulsa, Tulsa, Oklahoma; <sup>4</sup>National Renewable Energy Laboratory, Golden, Colorado.

One dimensional nanomaterials have attracted widespread attention since they provide the opportunity to study the effect of size and dimensionality on optical, magnetic and electronic properties. In this work we describe the growth and characterization of one-dimensional tungsten oxide nanorods. Tungsten oxide, in particular, has a vast range of applications as sensors, batteries, electrochromic materials and so on. The tungsten oxide nanorods were grown in hot filament chemical vapor deposition by electrically heating a tungsten coil in a mixture of hydrogen, methane and oxygen. The tungsten coil acted as both a heating source and a source for tungsten. Current was passed through the tungsten coil till it was white hot. The gases were passed through a water bubbler into quartz jar reactor. A blue or pale yellow powder of tungsten oxide (WO<sub>3</sub>) was deposited on the glass jar depending on the combination of the gases passed through the bubbler. Hydrogenated W<sub>18</sub>O<sub>49</sub> is formed when oxygen is passed through a water bubbler. When pure oxygen (in the absence of water vapor) was used, WO<sub>3</sub> was produced. The resulting deposits were characterized by Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), and Raman Spectroscopy. TEM showed the presence of nanorods with lengths less than 100 nm and diameter ranging from 5- 10 nm. The diameters were observed to be very uniform. Raman confirmed the presence of W-O bonds. We observed a shift in the Raman peak from 808 cm<sup>-1</sup> to 816 cm<sup>-1</sup>. The tungsten oxides were grown under varying conditions and characterized. These results will be discussed in greater detail.

3:45 PM [E7.6](#)

**Hot-wire Chemical Vapor Deposition of Crystalline Tungsten Oxide Nanoparticles.** [Archie H. Mahan](#), P. A. Parilla, K. M. Jones, R. Deshpande, S. H. Lee, L. M. Gedvilas and A. C. Dillon; NREL, Golden, Colorado.

Tungsten oxide (WO<sub>3</sub>) powders have been generated by the hot wire chemical vapor deposition technique where we heat a tungsten filament in a partial oxygen atmosphere in argon. After deposition, the powders are scraped off the walls of a quartz tube and are analyzed by x-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). TEM measurements on these powders have shown that they predominantly consist of nanorods, and occasionally nanotubes in addition to nanospheroids. The nanostructures are generally crystalline, and exhibit dimensions in the range of 10-200 nm, while the nanorods have 10 to 50 nm diameters and 50 to 200 nm lengths. Two sets of deposition conditions have been varied. In the first, the deposition pressure (P<sub>ch</sub>) was changed from 10 Torr to 150 Torr at constant deposition temperature (300C). We find that with increasing P<sub>ch</sub> the films change from being amorphous to highly crystalline. XRD and Raman results show that the latter films consist of the WO<sub>3</sub> monoclinic gamma and eta phases, and represent the first reports in the literature for highly crystalline bulk WO<sub>3</sub> nanoparticle synthesis. On the other hand, changing the deposition temperature at high P<sub>ch</sub> (150 Torr) changes only the ratio of the gamma to eta phases, and also influences the amount of W metal in the powder. Using certain deposition conditions (150 Torr, 300C), only the monoclinic gamma phase is deposited. Since WO<sub>3</sub> films for applications such as electrochromic windows (1) generally exhibit an oxygen deficiency (2), the stability of these films is monitored with respect to exposure to atmospheric contaminants. We present a model for why the films deposited at high P<sub>ch</sub> are crystalline and demonstrate the first deposition of crystalline nanorod

structures deposited without employing H<sub>2</sub>O as an oxidizer(3). (1). R. Deshpande et al., this conference. (2). S.-S. Sun and P.H. Holloway, J. Vac. Science Tech. A2, 336 (1984). (3). A.H. Mahan, P.A. Parilla, K.M. Jones, and A.C. Dillon, Chem. Phys. Lett. (in press)

4:00 PM [E7.7](#)

**Single-Step Biocatalytic Synthesis of Sexithiophene ( $\alpha$ -6T).** [Ramaswamy Nagarajan](#)<sup>1,2</sup>, [Subhalakshmi Nagarajan](#)<sup>2,1</sup>, [Jayant Kumar](#)<sup>1,2</sup>, [Lynne Samuelson](#)<sup>3</sup> and [Ferdinando F. Bruno](#)<sup>3</sup>; <sup>1</sup>Center for Advanced Materials, University of Massachusetts, Lowell, Massachusetts; <sup>2</sup>Departments of Physics and Chemistry, University of Massachusetts, Lowell, Massachusetts; <sup>3</sup>Nanomaterials Science Team, U.S Army Natick Soldier Center, Natick, Massachusetts.

$\pi$ -conjugated molecules such as thiophene oligomers are important organic semiconductors with potential applications in photovoltaic devices, semiconductor-based components including Schottky diodes and thin-film transistors. Among oligothiophenes,  $\alpha$ -6T (sexithiophene) has been reported to have mobilities of the order of 0.01 cm<sup>2</sup>/Vs. However, these mobilities are only attainable if the compounds are free of impurities. The conventional methods used for synthesizing  $\alpha$ -6T involve the use of ferric or cupric chloride to catalyze the oligomerization of thiophene. These methods often result in  $\alpha$ -6T with metal impurity that requires extensive purification. Here we report a method for the direct, one-pot synthesis of  $\alpha$ -6T that involves the enzyme catalyzed coupling of  $\alpha$ -terthienyl ( $\alpha$ -3T) [terthiophene]. The reaction is carried out in either a 50/50 acetone water system or in 60/40 water-dimethyl sulfoxide (DMSO) in the presence of sulfonated polystyrene and is catalyzed by oxidoreductases such as horseradish peroxidase (HRP). While  $\alpha$ -3T is quite soluble in solvents such as acetone and DMSO,  $\alpha$ -6T is only soluble in solvents such as mesitylene. This difference in solubility causes the precipitation of the product ( $\alpha$ -6T) while the catalyst (HRP) remains soluble in the reaction mixture. Matrix Assisted Laser Desorption Ionization (MALDI-TOF) spectroscopy of the product obtained from this reaction clearly indicates the formation of  $\alpha$ -6T. The nature and composition of the solvent mixture used in the synthesis is crucial in ensuring the facile isolation of the product. The solvent-system can be adjusted such that the sexithiophene formed, precipitates out of the reaction mixture. With appropriate control of the reaction and solvent conditions, this novel direct enzymatic route can serve as a convenient method for obtaining a purified form of sexithiophene. The detailed synthesis and characterization of  $\alpha$ -6T will be presented.

4:15 PM [E7.8](#)

**Proton conducting solid state organic/inorganic hybrids with self-assembling structures of heteropolyacids clusters.** [Itaru Honma](#) and [Masanori Yamada](#); ETRI, AIST, Tsukuba, Ibaraki, Japan.

Anhydrous proton conducting organic/inorganic hybrid electrolytes with self-assembling structure at nanoscale had been prepared by the mixing of organic polymer containing a phosphonic or sulfonic acid groups (PSS: polystyrenesulfonic acids) and 12-phosphotungstic acid (PWA), one of the heteropolyacid families. The proton conductivity and thermal stability of organic/inorganic hybrid materials increased with the mixing ratio of heteropolyacid. Maximum proton conductivity of organic/inorganic hybrid membrane was found to be 1x10<sup>-2</sup> S cm<sup>-1</sup> at 180C under anhydrous condition. Additionally, the fuel cell test of hybrid material using a dry H<sub>2</sub>/O<sub>2</sub> showed the power generation at 160C under anhydrous conditions. In this contribution, a potential of novel anhydrous proton conducting organic/inorganic hybrid materials for application to solid state electrochromic devices as well as polymer electrolyte membrane fuel cells (PEFC) operated at anhydrous and intermediate temperature (100 - 200C) conditions is discussed.