

## Topical Symposia

### Room Town & Country A - Session TS1-1-MoM

#### Coatings for Energy Storage and Conversion - Batteries and Hydrogen Applications I

**Moderators:** Dr. Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, Klaus Böbel, Bosch Manufacturing Solutions, Germany

10:00am **TS1-1-MoM-1 The Effect of Microstructure on the Hydrogen Storage Capacity of  $Ti_xZr_{1-x}$  Thin Films**, *Ido Zukerman, M. Buzaglo*, Division of Chemistry, NRCN, Israel; *S. Hayun*, Department of Materials Engineering, Ben Gurion University of the Negev, Israel

Metal hydrides ( $MH_x$ ) provide a promising solution for a future hydrogen-based energy system due to their high hydrogen storage density and safety advantages compared to compressed or liquefied hydrogen. Thin films were proposed to ease the absorption/desorption cycles by maximizing the surface-to-volume ratio. In this study, we suggest controlling the macro- and micro- structure of  $Ti_xZr_{1-x}$  thin films, in order to reduce the absorption/desorption temperature and to increase the rate and absorbed hydrogen volume. To achieve this goal, a series of  $Ti_xZr_{1-x}$  thin films were deposited using pulsed-DC magnetron co-sputtering technique. Low sputtering power, high working pressure, or floating bias conditions resulted in an open columnar structure (i.e., zone 1 microstructure). High negative bias ( $< -150$  V), however, promoted a dense columnar structure (i.e., zone T microstructure). The thin film's hydrogenation was conducted as follows: The samples were held at 623 K under vacuum ( $< 5 \times 10^{-3}$  Pa) for 1 hr for surface activation, then the chamber was filled with pure hydrogen to  $2.0 \pm 0.1 \times 10^4$  Pa and cooled to room temperature. The samples were held under  $H_2$  for additional 24 hours at room temperature. Temperature-Programmed Desorption (TPD), Glow Discharge Spectroscopy (GDS), and electron microscopy were used to study the microstructure of the films, hydrogen storage capacity, desorption temperature, and the durability for multiple absorption/desorption cycles.

10:20am **TS1-1-MoM-2 Transition Metal – Doped Ni/YSZ Anode Functional Layers for Solid Oxide Fuel Cells Produced via Magnetron Sputtering**, *K. Steier*, Manchester Metropolitan University, UK; *I. Jang, A. Hankin*, Imperial College London, UK; *P. Kelly, Justyna Kulczyk-Malecka*, Manchester Metropolitan University, UK

Solid oxide fuel cells (SOFCs) convert the chemical energy stored in fuels, such as hydrogen and gaseous hydrocarbons, directly into electrical power and thermal energy through electrochemical reactions. State-of-the-art SOFC anodes consist of a cermet of nickel and yttria-stabilised zirconia (YSZ) to increase the reactive sites at the anode/electrolyte interface, generating so-called triple-phase boundaries. The quantity of triple-phase boundaries in nanostructured materials increases through finer particle sizes, resulting in enhanced performance. For that reason, the magnetron sputtering technique, which offers elemental distribution at the nanoscale, high deposition rates, reproducibility, scalability and excellent uniformity over large-area substrates has been chosen as the deposition method to fabricate anode functional layers (AFLs) for SOFCs.

Nanostructured NiO-YSZ thin films have been previously produced by reactive pulsed DC magnetron co-sputtering of metallic targets of zirconium-yttrium and nickel, defining the optimal deposition parameters to create state-of-the-art AFLs. Based on recent studies, the future of oxide-based anode materials for SOFCs will greatly focus on reducing Ni catalyst content through alternative non-precious metal doping and increasing the cell performance by tailoring the microstructure of the AFL. This would allow Ni coarsening to be mitigated and maintain the nanostructure over the lifetime of the cell. Therefore, in this study complex transition metal oxides, such as vanadium, tantalum or manganese oxides, were doped into SOFC anodes to study their influence on the structural and morphological properties of magnetron sputtered AFLs. The effect of the dopant's concentration on the properties of Ni-YSZ films in as-deposited, pre-annealed and reduced state was analysed using SEM, EDS, XRD and XPS. To characterise the electrochemical performance of the deposited films, polarisation curves were obtained from SOFC single stack assemblies under hydrogen and air flows for anode and cathode, respectively, at operating temperatures of 750, 800 and 850 °C.

10:40am **TS1-1-MoM-3 Surface Modification of Graphite Felt Electrode for Vanadium Redox Flow Batteries by High Entropy Alloy Oxide Thin Films: Effect of Oxygen Gas Flow Ratios**, *Krishnakant Tiwari, C. Wang*, National Taiwan University of Science and Technology, Taiwan; *B. Lou*, Chang Gung University of Technology, Taiwan; *J. Lee*, Ming Chi University of Technology, Taiwan

Vanadium redox flow battery (VRFB) is one of the most promising renewable large scale energy storage devices. Electrode is one of the key components of VRFB which has significant effect on the energy efficiency and cost of the system. Carbon-based materials are widely used as electrodes in VRFB due to their lower electrical resistance and better corrosion resistance. However, untreated carbon-based electrode shows poor catalytic activity for redox reaction towards vanadium ions and cannot meet the development needs of VRFB. Among several surface modification methods, deposition of nanoparticles on the graphite felt (GF) electrode has been widely used. However, the poor uniformity of deposited nanoparticles results in a low charge transfer rate and poor adhesion. In this work, we investigated a surface modification approach for the graphite felt electrode by depositing refractory VNbMoTaW high entropy alloy oxide (HEAO) films grown under different oxygen flow rates using a high power impulse magnetron sputtering (HiPIMS) system for improving the performance and economic competitiveness of VRFB. Surface morphology of HEAO modified GF electrodes were examined using FESEM, contact angle test, Raman analysis, XRD and XPS. The electrochemical performances of GF electrodes modified with HEAO films grown under different oxygen gas flow ratios were compared. The flow cell test of HEAO modified GF electrodes was performed to demonstrate the charge-discharge capacity, voltage efficiency and energy efficiency at different current densities. The cycling test illustrated the stability of the VNbMoTaWOx film layer on graphite felt, where no significant decay in efficiencies was observed. The effect of oxygen gas flow ratios on the phase, chemical compositions, and electrochemical performance of the HEAO films were also discussed.

11:00am **TS1-1-MoM-4 Temperature Dependency of Specific Electrical Conductivity of DLC Coatings**, *S. Danningner*, University of Applied Sciences Upper Austria; *Francisco Delfin*, University of Applied Sciences Upper Austria, Argentina; *C. Forsich, D. Heim, M. Schachinger*, University of Applied Sciences Upper Austria; *B. Rübiger, C. Dipolt, T. Müller*, Rubig GmbH & Co KG, Austria

DLC coatings show a favourable combination of both low friction coefficient and high wear resistance and are therefore widely used for technical applications. To increase the film's electrical conductivity for special applications (e.g., coatings for electrodes) common methods are film doping with nitrogen or metals. This study, however, investigates the decrease of electrical resistivity of un-doped DLC coatings through an increase in deposition temperatures above 450 °C.

DLC coatings were produced by means of PA-CVD using pulsed DC discharge. Temperatures of 450 °C, 500 °C and 550 °C were used to deposit a-C:H and a-C:H:Si films on various steel substrates. Process gas consisted of a mixture of argon, acetylene, and HMDSO as silicon precursor. Additionally, coatings with process gas consisting of 20 % hydrogen were produced respectively. Afterwards, for coatings deposited at 450 °C a tempering was conducted at 550 °C to exclude only heat treatment related effects. An amorphous silicon interlayer was used as an electric insulator between substrate and coating. To measure the specific electrical resistivity of all coatings the van der Pauw method employing four contact points was performed. Further coating characterizations included GDOES and EDX analysis and the measurement of layer hardness through nanoindentation. Raman spectroscopy was performed, and the spectra were compared to estimate the hydrogen content and hybridization of the DLC coatings.

Silicon free DLC films showed a clear decrease of specific electrical resistivity with an increase of deposition temperature. Values dropped from  $10^7 \mu\Omega \text{ cm}$  at 450 °C to under  $10^4 \mu\Omega \text{ cm}$  at 550 °C, reaching levels comparable to graphite. While the specific electrical resistivity of these a-C:H films decreased with higher deposition temperatures, a hardness increase of more than 70 % was measured over the temperature range. The average hardness of 350 HV at 450 °C rises to 600 HV for 550 °C. Process gas consisting of 20 % hydrogen decreased specific electrical resistivity even more by at least 60 %, while also slightly raising surface hardness. For a-C:H:Si coatings the specific electrical resistivity exceeded the measurement setup's detection limit of about  $1.9 \cdot 10^7 \mu\Omega \text{ cm}$ , as they seem to be highly electrically insulating. Hydrogen containing process gas did not show any effects on silicon doped coatings. With this new process approach electrically conductive and hard a-C:H coatings could be

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produced without metal- or nitrogen-doping with thicknesses up to 120  $\mu\text{m}$  only through an increase of deposition temperature.

11:20am **TS1-1-MoM-5 High Efficiency of Metal Oxide Catalysts for Vanadium Redox Flow Battery, *Chen-Hao Wang***, National Taiwan University of Science and Technology, Taiwan **INVITED**

The development of sustainable energy resources such as wind and solar is urgently needed to diminish the environmental impact of fossil fuels. Nevertheless, energy storage systems (ESS) are required to store and stabilize such intermittent and random clean energy sources. Among various energy storage devices, the vanadium redox flow battery (VRFB), first invented by Skylla-Kazacos and co-workers in the 1980s, is one of the most promising large-scale energy storage devices owing to its design flexibility, extended cycle life, and safe operation. Furthermore, VRFB avoids cross-contamination due to employing the same electroactive element (vanadium) for both half-cells. VRFB comprises three essential components: membrane, electrolyte, and electrode. To store energy, it uses the redox couples of the electrolyte,  $\text{V}^{3+}/\text{V}^{2+}$  and  $\text{VO}^{2+}/\text{VO}_2^+$ , on the negative and positive sides, respectively. The membrane behaves as a separator for the two half-cells and maintains electroneutrality by passing hydrogen ions through it. The electrode does not participate in the redox reaction but provides a reaction site for active species. Therefore, some active electrodes with metal oxide-based catalysts are used in the VRFB to enhance performance. In this talk, we will introduce metal oxides, e.g.,  $\text{W}_{18}\text{O}_{49}$ ,  $\text{CeO}_2$ , and  $\text{BiVO}_4$ , which have excellent electrochemical activities, making VRFB more powerful.

**Keywords:** Energy storage system, vanadium redox flow battery (VRFB), electrode modification, energy efficiency

12:00pm **TS1-1-MoM-7 Effect of Mg Doping on Characterization and Cycling Performance of  $\text{LiCoO}_2$  Thin Film Cathode for Lithium-Ion Batteries, *Tai-Yan Liu, J. Huang, C. Liu***, National Cheng Kung University (NCKU), Taiwan

Lithium-ion batteries (LIBs) are the most popular energy storage devices for portable electronics and electric vehicles due to their high energy density, long cycling lifetime and no memory effect. Lithium cobalt oxide ( $\text{LiCoO}_2$ , LCO) is the first commercialized cathode materials for LIBs. It has many advantages such as favorable rate capability, excellent capacity retention, and high theoretical specific capacity compared with other cathode materials. However, LCO has severe structural destruction due to irreversible phase transition under high cut-off voltage above 4.2V, which causes rapid capacity fading and structural instability during repeated cycling. Therefore, electrochemically inactive element doping is studied to improve structural stability. Among many dopants, Mg is regarded as a promising element to achieve better cycling performance for LCO. Hence, we deposited Mg-doped lithium cobalt oxide (Mg-LCO) thin films for cathode materials. Co-sputtering method and post annealing were utilized to grow Mg-LCO thin films. Firstly, Al foils were sequentially cleaned in 95% ethanol and DI water for 10 min, respectively. Secondly,  $\text{LiCoO}_2$  (99.99%) and MgO (99.99%) targets were co-sputtered via RF magnetron sputtering system to deposit Mg-LCO thin films on Al foils at 250  $^\circ\text{C}$  for 60 min in  $\text{Ar}/\text{O}_2$  mixed gas atmosphere. The RF power of the  $\text{LiCoO}_2$  target was fixed to 100W and the RF power of the MgO target was varied from 0 to 60W. Afterwards, the Mg-LCO thin films were annealed at 600 $^\circ\text{C}$  in air for 4h via a tube furnace. From XPS and sheet resistance measurement, Mg successfully doped into LCO thin films and replaced Li sites thereby increasing the sheet resistance. SEM images showed granular size and thickness in the Mg-LCO films decreased with the MgO working power from 0 to 60W. TEM and XRD investigations revealed that the Mg-LCO thin films were layered structure and polycrystalline with (003) preferred orientation. Finally, in half-battery test, the 60W Mg-LCO thin film cathode exhibited better voltage plateaus and capacity retention than 0W, 30W Mg-LCO in the voltage range of 3.0-4.2 V at 0.2 C rate after 30 cycles. According to the above results, the structure of LCO thin film after Mg doping was more stable during charge/discharge process. In future, we will study the electrochemical performance of LCO thin films with higher Mg doping amount. Further, we will do the high voltage cycling tests (above 4.5V) and combine electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) to investigate redox kinetics of high voltage Mg-doped  $\text{LiCoO}_2$  thin film cathode.

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