Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-1-MoM

Coatings for Batteries and Hydrogen Applications I

Moderators: Chen-Hao Wang, National Taiwan University of Science and Technology, Taiwan , **Martin Welters**, KCS Europe GmbH, Germany, **Fan-Bean Wu**, National United University, Taiwan

10:00am **TS1-1-MoM-1 Hydrogen Technology – Which Role Play Thin Films on the Performance and Sustainability?**, ***Christina Scheu [scheu@mpie.de]***, Max-Planck-Institut for Sustainable Materials, Germany **INVITED**

Hydrogen technology is an important route to an environmental friendly economy. It includes the generation of green hydrogen via (photo)electrochemical cells, the efficient storage and transport of hydrogen in (often) metallic gas tanks and pipelines and the usage in fuel cells to power trucks and cars. Thin films play a crucial role in transitioning from conventional power systems to this value-added chain. In the presentation, different examples will be given to demonstrate the necessity of thin film development for hydrogen technology. For example, hydrogen is stored and transported often in expensive steel containers and pipelines, but a protective coating made by e.g. Al_2O_3 on cheaper steels can sufficiently prevent hydrogen ingress. In photoelectrochemical cells, thin absorber thin films (often only a few tens of nanometer thick) allow to absorb a high amount of visible light and generate electron – hole pairs which are used to split water into hydrogen and oxygen. Typical examples for excellent absorber thin films are based on Sn doped Fe_2O_3 or $BiVO_4$, but further development is needed to make them even more efficient. Thin films are also used in fuel cells, not only as corrosion protector for the metallic flow field where hydrogen and oxygen are distributed, but also in the protection of catalyst and support material to prevent their degradation. An important role is also the development of novel catalyst for fuel cells or electrolyzer with excellent longevity by investigating thin film model catalyst where the impact of the chemical composition and crystal structure can be systematically evaluated. In all the examples, defects such as grain boundaries or stacking faults within the thin film are crucial for the performance and lifetime, and they need to be analysed down to the atomic scale. In our work we use aberration corrected (scanning) transmission electron microscopy and atom probe tomography to get insights in the thin film structure and defects.

Acknowledgment: The author is grateful to all the colleagues and co-workers who contributed to the different aspects of the hydrogen technology projects and to financial support from the German Science Foundation (DFG) within the CRC 1625 and the Federal Ministry for Economic Affairs and Climate Protection (BMWK) within the project PAULL1/2.

10:40am **TS1-1-MoM-3 Thin Film Ceramic Layers Enabling Lightweight Solid Oxide Fuel Cell for Aviation Application**, ***Vignesh Ahilan [vignesh.ahilan@airbus.com]***, *Pedro Nehter, Helge Geisler,* Airbus Operations GmbH, Germany*; Oliver Rohr, Christian Metzner,* Airbus Defence and Space GmbH, Germany

Airbus is developing the world's first hydrogen based commercial airplane within the ZEROe program. The idea of ZEROe is the decarbonization of the aviation industry. Although the most established and matured fuel cell type is the proton exchange membrane (PEM) technology, Airbus Central Research and Technology (CRT) is looking at Solid Oxide Fuel Cell (SOFC) concepts for prospective propulsion technology. The SOFC system is an attractive candidate for aircraft application due to its capability of high efficiency when combined with gas turbine engines and also fuel versatility. SOFCs currently dominating the market feature planar cell and stack designs, primarily targeting stationary applications. These cells are predominantly manufactured using traditional ceramic processing technologies. However, the conventional manufacturing methods present limitations when it comes to producing high performing lightweight SOFCs based on thin film ceramics, highlighting a need for futuristic fabrication techniques to advance this promising technology.

Using a novel manufacturing approach, specifically a sequential dip-coating technique, we have developed a lightweight anode supported tubular SOFC featuring 8 µm thin-film 8YSZ electrolyte. This promising tubular SOFC has achieved an experimentally tested gravimetric power density of approximately 2 kW/kg with dual end current collection method under high fuel utilization conditions. In the next development stage, we are engineering an electrically serial-networked electrolyte supported SOFC that incorporates a 1-2 µm dense thin-film Gadolinium-doped Ceria (GDC) barrier layer. This electrical networked SOFC design offers a theoretical estimated power density exceeding 3 kW/kg. Additionally, we will explore automated ultrasonic spray coating techniques to develop continuous, uniform thin-film ceramic coatings for SOFCs. This strategic approach, combining innovative production methods for developing thin-film ceramic layers, paves the way for fabricating weight-optimized high performance SOFCs tailored for aviation applications.

11:00am **TS1-1-MoM-4 Low-Temperature Sintering of $Li_7La_3Zr_2O_{12}$ (LLZO) Electrolyte Coatings by the Sol Impregnation Method for All Solid-State Lithium-Ion Batteries**, ***Yen-Yu Chen [yychen@mail.npust.edu.tw]***, *Guang-Yi Yao, Shao-Chien Tai,* National Pingtung University of Science and Technology, Taiwan

All solid-state lithium-ion batteries (ASSLIBs) have attracted attention from academics and industries due to the safety issues and high efficiencies. Among kinds of the electrolyte materials for ASSLIBs, the oxide-based electrolytes show high electrical conductivities and electrochemical stabilities and are one of the potential materials for the solid electrolyte of ASSLIB. $Li_7La_3Zr_2O_{12}$ (LLZO) is one of the oxide-based electrolyte materials and was developed in our previous investigation. After sintering at 1100℃ for 12 h, significant interdiffusion between the LLZO electrolyte coatings and the LCO cathode was observed, and second phases were also formed between the LLZO coatings and LCO substrates that inhibited the electrical performance of LLZO-based ASSLIBs. In this study, we try to reduce the sintering temperature to less than 1000℃ to prevent the over-diffusion between LLZO coatings and LCO-based substrates. A sol impregnation method was taken to fill the pores in the pre-sintered LLZO coatings and densify the coating samples at a temperature lower than 1000℃. Several techniques were taken to analyze the LLZO coating samples, including crystalline phases by X-ray diffraction (XRD), the microstructures by scanning electron microscopy (SEM), the elemental distribution mapping by scanning transmission electron microscopy (STEM), and electrical performance analysis by electrochemical impedance spectrum (EIS). The results show that by the LiOH sol impregnation, the densities of the LLZO coating layers can be significantly increased after sintering at 1000℃ for 12 h, as well as the electrical performance of the semi-cells. The details of the interface diffusion phenomena between LLZO coatings and LCO substrates after low-temperature sintering will be shown in the presentation.

11:20am **TS1-1-MoM-5 PVD-synthesized Nitrides as Hydrogen Barrier Coatings**, ***Phillip Rückeshäuser [phillip.rueckeshaeuser@tuwien.ac.at]***, TU Wien, Austria*; Szilard Kolozsvari, Peter Polcik,* Plansee Composite Materials GmbH, Germany*; Timea Stelzig,* Oerlikon AM Europe GmbH, Germany*; Konrad Fadenberger,* Oerlikon Balzers Coating Germany GmbH, Germany*; Klaus Boebel,* Oerlikon Balzers, Liechtenstein*; Tomasz Wojcik, Helmut Riedl,* TU Wien, Austria

Hydrogen-based energy systems require materials that are resilient to the reactive nature of hydrogen. This is important due to phenomena such as hydrogen embrittlement and corrosive attacks, which are common in fuel cells and electrolyzers. One potential solution to mitigate material deterioration is the use of physical vapor deposition (PVD) synthesized hydrogen-resistant barrier coatings on exposed surfaces.

Currently, investigations into hydrogen permeation for bulk materials are primarily conducted using either pressurized or electrochemical testing methods. The electrochemical method, while offering advantages such as versatility and simplicity, is mostly applied to bulk materials and seldom used for thin film materials. Therefore, it is important to establish electrochemical permeation testing methods for coating materials as well. In this study we investigated the hydrogen permeation characteristics of the well-known coating systems TiN and CrN deposited on unalloyed ferritic steel substrates via sputter deposition and cathodic arc evaporation. These samples were electrochemically charged in a Devanathan-Stachursky permeation cell and parameters like diffusion coefficients, hydrogen fluxes and permeation reduction factors have been determined. Additionally, these results were correlated with the coating's microstructure, obtained from scanning and transmission electron microscope and linear sweep voltammetry.

Our results indicate that both the deposition process and coating morphology significantly influence the permeation characteristics of the material. These findings on well-known nitride-based material systems could assist in engineering hydrogen barrier coatings for various future applications.

11:40am **TS1-1-MoM-6 Porous W2N Fibrous-Nanograins and TiN Nanopyramids Framework for High Energy Density Flexible Asymmetric Supercapacitors**, ***Rajesh Kumar [r_kumar@ph.iitr.ac.in],*** Indian institute of technology Roorkee, India*; Bhanu Ranjan, Davinder Kaur,* Indian Institute of Technology Roorkee, India

Enhancing the energy density of flexible asymmetric supercapacitors (ASCs) necessitates developing and implementing high-performance anode materials for technological developments in wearable energy storage systems. Tungsten nitride (W_2N) offers enormous potential as an anode material for ASCs, ascribed to its substantial specific capacitance, massive electrical conductivity, and extended negative potential window. In this work, we fabricated a durable coin cell and flexible ASC utilizing W_2N/SSM fibrous-nanograins anode and TiN/SSM nanopyramids cathode deposited over flexible stainless steel mesh (SSM) substrate by the DC magnetron sputtering technique. The W_2N/SSM//TiN/SSM ASC device demonstrates a high areal capacitance of 21.3 $mF.cm^{-2}$ operating across a wide and stable electrochemical voltage window of 1.3 V with outstanding cycling robustness demonstrating 89.09% retention over 8000 charge-discharge cycles. Notably, the ASC achieved a high energy density of 34.33 $mWh.cm^{-3}$ and a high power density of 17.32 $W.cm^{-3}$. The persistent electrochemical performance of ASC is mainly attributed to the dominance of surface-controlled capacitive and pseudocapacitive charge storage kinetics of W_2N/SSM for Na^+ ions comprehensively examined employing 3D Bode and Dunn's techniques. The flexible ASC shows remarkable mechanical stability of 92.36% up to 500 bending cycles. This study establishes W_2N nanograin's potential as a high-energy anode material, revealing the capability to increase the effectiveness of ASC for portable and miniaturized energy storage devices.

12:00pm **TS1-1-MoM-7 Nitride and Amorphous/Crystalline Multilayers as Hydrogen Permeation Barriers**, ***Balint Istvan Hajas [balint.hajas@tuwien.ac.at]***[1], TU Wien, Institute of Materials Science and Technology, Austria*; Vincenc Nemanič, Marko Žumer, Ardita Kurtishaj Hamzaj,* Jožef Stefan Institute, Slovenia*; Alexander Kirnbauer, Tomasz Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; Szilard Kolozsvari,* Plansee Composite Materials GmbH, Germany*; Paul Heinz Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Hydrogen permeation presents a key obstacle to the deployment of hydrogen-based energy systems, necessitating robust coatings that act as permeation barriers. In this study, we investigate nitride-based monolithic and multilayer (ML) coatings deposited by magnetron sputtering as hydrogen permeation barriers (HPBs). Coating systems including TiN, (Ti,Al)N, MoN/TaN, and Si–B–C–N–O, as well as TiN/AlN and Si–B–C–N–O/TiN MLs, were synthesized and characterized by XRD, SEM, TEM, and nanoindentation. Their efficiency as HPB was evaluated on films deposited on Eurofer 97 substrates using the gaseous hydrogen permeation method at 400°C.

Monolithic crystalline coatings exhibited limited barrier properties, with TiN reaching a PRF of ~190 and (Ti,Al)N failing due to microstructural defects induced by high deposition bias. Crystalline MLs demonstrated that coherent fcc–fcc interfaces in TiN/AlN with a bilayer ratio Γ = 2:1 (2 nm TiN and 1 nm AlN) effectively suppress permeation by combining nearly epitaxial interfaces with interruptions of columnar growth, which block fast diffusion pathways, leading to a PRF above 20,000. In contrast, thicker AlN layers relaxed into hcp-AlN, disrupting coherency and providing diffusion paths. The MoN/TaN system showed only moderate resistance (PRF ~50). Amorphous Si–B–C–N–O already exhibited excellent barrier performance (PRF >1000) by eliminating grain and specifically column boundaries, which was further improved through the incorporation of TiN. In particular, the $\Gamma_{Si–B–C–N–O/TiN}$ = 2:3 multilayer reached PRF values of ~5300 by embedding crystalline TiN within amorphous Si–B–C–N–O layers, yielding a dense, columnar-free architecture without continuous diffusion channels. These findings underscore that hydrogen permeation resistance can be maximized either by coherent interface stabilization or by amorphous/crystalline alternation, highlighting interface engineering and microstructural control as decisive design principles for next-generation energy technologies.

[1] **Graduate Student Award Finalist**

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