

Topical Symposium on Sustainable Surface Engineering Room Town & Country B - Session TS1-2-MoA

Coatings for Batteries and Hydrogen Applications II

Moderator: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany

2:00pm **TS1-2-MoA-2 Effect of Atomic Layer Deposited Films on Three-Dimensional Electrodes for Lithium-Ion Batteries**, P. Lin, National Chung Hsing University, Taiwan; **Chih-Liang Wang** (wangcl@mx.nthu.edu.tw), National Tsing Hua University, Taiwan

The great capability of atomic layer deposition (ALD) in precisely controlling the film quality, such as thickness, composition and conformality has been paid much attention. Herein, we presented a study of coating nanocomposite metal oxides via ALD on three-dimensional electrodes for lithium-ion batteries. The three-dimensional electrodes were prepared by the hydrothermal synthesis of TiO₂ nanorods on carbon cloths. The nanocomposite metal oxides of TiO₂ and ZnO were deposited on TiO₂ nanorods by ALD. The effect of metal oxides on electrochemical performance was systemically investigated by using different ALD cycles of TiO₂ and ZnO. The results indicated that the reversible capacity and rate performance of three-dimensional electrodes can be improved after ALD nanocomposite metal oxides. The improved performance can be attributed to the function of ALD TiO₂ to not only alleviate the volume change and the growth of solid electrolyte interphase but also improve electronic conductivity. More details related to battery performances and film properties, influenced by the ALD cycle of individual metal oxide, will be reported in the presentation.

2:20pm **TS1-2-MoA-3 Effects of Additives on Electrochemical Performance of Sodium Ion Batteries**, Ting Ching Lin (tim881231@gmail.com), J. Huang, National Cheng Kung University (NCKU), Taiwan; C. Chang, National University of Tainan, Taiwan

In recent years, the surge in electric vehicle popularity and the push for renewable energy development by various governments globally have enhanced energy security, mitigated the risk of fuel leaks, and lessened the dependence on imported fuels. This has been achieved by ensuring a steady supply of electricity and diversifying fuel sources. As the demand for lithium continues to rise with the increased adoption of lithium-ion batteries, attention is turning towards sodium ion batteries due to the limited availability of lithium resources. Sodium ion batteries are gaining traction, particularly in the electrical and electronic sectors. Their operational principle closely mirrors that of lithium-ion batteries, encompassing positive and negative electrodes, isolation membranes, and electrolytes. Notably, sodium ion batteries offer cost advantages over lithium batteries, with more readily available precursor materials for the negative electrode and a lower carbonization temperature during graphite negative electrode production. Despite these merits, sodium ion batteries currently encounter challenges, such as lower energy density and storage capacity compared to lithium batteries. The cycle life of existing sodium ion batteries also falls short of that seen in commercial lithium batteries. The primary hurdles stem from the lower energy density and suboptimal cycling performance, which heavily rely on the formation of solid electrolyte interface (SEI) films on the electrode surface.

To address these challenges, the research proposes a novel approach: the combination of different kinds of new ion additives to form a composite additive. The aim is to create a stable and dense SEI that exhibits thinness, electronic insulation, and ion conductivity. This approach seeks to overcome the limitations of sodium ion batteries, particularly their low energy density and poor cycling performance, by fostering the development of an enhanced SEI.

In this research, we used electrochemical impedance spectroscopy (EIS) to measure interface resistance, and used X-ray photoelectron spectroscopy (XPS), Scanning Electron Microscope (SEM), Fourier-transform infrared spectroscopy (FTIR) to observe the electrode surface and analyze the SEI film. The results indicate that the addition of the NaDFP ionic additive effectively improves the retention of battery capacity and establishes a durable SEI film.

Keywords: sodium ion batteries, new ion additives

2:40pm **TS1-2-MoA-4 Effect of SiO_x/RGO via Phosphorus Doping as Anode Materials for Lithium-Ion Batteries**, Wen-Feng Lin (chanes40417@gmail.com), J. Huang, S. Brahma, National Cheng Kung University (NCKU), Taiwan; Y. Shen, Hierarchical Green-Energy Materials Research Center (Hi-GEM), Taiwan

Lithium-ion batteries has been one of the promising energy storage devices due to its high energy density, high capacity, and non-memory effect. Anode is one of the important component of the batteries. To meet the demand of electronic devices, scientists are dedicated to develop novel anode materials since the traditional graphite has the drawback of low theoretical capacity (approximately 372 mAhg⁻¹), which cannot achieve the requirement of the high-energy devices. There are different types of materials during lithiation/delithiation process, such as alloys, transition metals, and insertion/desertion materials. Among them, we choose non-stoichiometric silicon oxide (SiO_x, 0 < x < 2) because it has relatively low volume expansion as compared to pure silicon. However, the ratio of volume expansion is still a non-negligible phenomenon since it indirectly affects the capacity. Therefore, we utilize the characteristics of reduced graphene oxide (rGO) and phosphorus (P) to improve the disadvantages of SiO_x. The character of rGO is the carrier of lithium ions and electrons owing to the 2D-layered structure. Besides, rGO is a carbonaceous material which can enhance the conductivity of anode materials. For the purpose of improving initial coulombic efficiency (ICE), P acts as dopant that can create extra space for lithium-ion storage and transport because the chemical and physical structures of rGO may be changed. We first synthesize SiO_x/rGO, then modify the composite with P by using phosphoric acid as P source in the second step followed by post annealing as the last step. The final product is named as P-SiO_x/rGO (1P, 2P represent different concentration of phosphoric acid). From the results of XPS, P bond with O and EDS mapping shows the uniform distribution of P. Hence, the analyzed results ensure the doping of P. Further, the electric properties are verified through the testing of battery performance, charge/discharge, cycling and C-rate are included. Compared to the un-doped and doped samples, ICE of the latter (42.5 % for 1P-SiO_x/rGO and 56.2 % for 2P-SiO_x/rGO) are higher than the former (39.7 % for un-doped SiO_x/rGO), which means the effect of P is achieved. On the other hand, P-doping also stabilized the structure of electrode, the lithiation capacity of 1P-SiO_x/rGO and 2P-SiO_x/rGO retain a value of 340 and 424 mAhg⁻¹, respectively at 0.1 Ag⁻¹ after C-rate testing, while 291 mAhg⁻¹ for the un-doped electrode, indicating an enhancement of the cyclability and rate performance of the composite.

3:00pm **TS1-2-MoA-5 The Research of Different Pre-Lithiation Methods to Enhance Coulombic Efficiency of SnO₂ Modified TiO₂ as Anode Material in Lithium-Ion Battery**, Cheng-Hsun Ho (n56124032@gs.ncku.edu.tw), J. Huang, National Cheng Kung University (NCKU), Taiwan; Y. Shen, Hierarchical Green-Energy Materials Research Center (Hi-GEM), Taiwan

Lithium-ion batteries have been widely applied in our daily lives and there is an ongoing demand for LIB with higher energy density, lower self-discharge, longer cycling life and better safety. Titanium dioxide (TiO₂) has emerged as a highly promising anode material for lithium-ion batteries due to its remarkable cycling stability, impressive rate performance, cost-effectiveness, and environmental friendliness. Nevertheless, the main obstacles associated with this material include its limited electronic/ionic conductivity and lower theoretical capacity. In order to overcome this issue, our research has been modifying high-capacity material (e.g., SnO₂) into TiO₂ with an eye to promoting its theoretical capacity. Modifying SnO₂ into TiO₂ reduces the impedance and increases the Li-ion diffusion rate. The SnO₂/TiO₂ composite is synthesized by the chemical bath with Sn(BF₄)₂, HBF₄, Na₂S₂O₃ and TiO₂ (rutile and anatase mixed phase) followed by annealing at different temperature. From the TEM and XRD results, the SnO₂/TiO₂ composite had been successfully synthesized. It can be inferred from the figure that the structure of the composite might be the shell of the SnO₂ & TiO₂ solid solution while the core remains TiO₂ structure. However, the table below shows the serious fading problem of SnO₂/TiO₂ composite with different annealing temperature during the first and second cycle. Active lithium loss (ALL) in the initial lithiation process causes irreversible capacity of LIBs due to the formation of unstable solid electrolyte interface (SEI) layer on the electrode surface. To resolve the problem, pre-lithiation has been widely accepted as one of the most promising strategies to compensate for active lithium loss. Our group have been dedicated to trying various pre-lithiation techniques, such as electrochemical and thermal evaporation of lithium. Electrochemical pre-lithiation aims to generate stable SEI layers by applying constant voltage while lithium evaporation deposition involves depositing various thickness of lithium to achieve different levels of pre-lithiation. The ultimate goal

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would be giving out advantages and challenges of each one then finding out the optimal approach to improve cycling performance of tin-based anodes in lithium-ion batteries.

3:20pm **TS1-2-MoA-6 Study on the Characteristics of Garnet-Type Solid Electrolytes in Lithium Metal Solid-State Batteries with Multilayer Interfaces**, *Hung-Ju Chen (m46111060@gs.ncku.edu.tw)*, J. Hung, S. Lin, National Cheng Kung University (NCKU), Taiwan

Lithium-ion batteries (LIB), which is a rechargeable battery, mainly used in related electronics industries, such as transportation vehicles, medium to large uninterruptible power systems (UPS), solar systems, energy storage systems, electric hand tools, aerospace equipment, power battery market and aviation battery. The LIB life would decrease with increasing in the number of charge and discharge cycles. Besides, the risk of LIB electrolyte is a liquid organic solvent, which is easy to burn and explode in case of fire. Recently, solid-state electrolytes have attracted attentions and show the many advantages including high safety, high energy density, and greater temperature tolerance. Among different types of solid-state electrolytes, garnet-type LLZTO ($\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$) electrolyte has high ionic conductivity (10^{-3} to 10^{-4} S / cm) and chemical stability towards lithium metal. However, lithium dendrites will be generated during the charge and discharge process of solid electrolyte batteries. The dendrites could lead to short circuit and failure of battery. Moreover, poor contact in the interface between solid electrolyte and lithium metal could cause the increased impedance and decreased conductivity. The aim in this study is to use different types and proportions of metal fluorides to modify the interface; meanwhile, the interface forms an electronically insulating and lithium-friendly lithium fluoride layer to promote the chemical diffusion of lithium in lithium metal alloys and reduce interface impedance. After the project, we expect that a new generation of lithium metal solid-state batteries will be developed.

4:20pm **TS1-2-MoA-9 Investigation of Y-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (Y-LLZO) Coatings by Colloidal Coating Process for the Electrolyte of all Solid-state Battery**, *Yen-Yu Chen (yychen@mail.npust.edu.tw)*, G. Yao, National Pingtung University of Science and Technology, Taiwan; X. Yan, Chinese Culture University, Taiwan

Lithium ion batteries (LIBs) were widely applied on computer, communications, and consumer electronics for decades, as well as on the electric vehicles in recent years. Due to the risks of liquid electrolytes for current LIBs, solid state electrolytes for LIBs were investigated. In this study, Y-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (Y-LLZO) materials were prepared by a solid-state reaction method. After well-dispersed, Y-LLZO coatings were deposited on the LiCoO_2 /Y-LLZO composite anode from the Y-LLZO suspensions by a spin-coating method. The crystal phase analysis by the X-ray diffraction (XRD) method shows, the cubic perovskite phase of Y-LLZO can be obtained after calcined at 900°C for 12 h. The grain size of the Y-LLZO powders observed by the scanning Electron Microscopy are most within several μm . The crystal phase of the Y-LLZO samples after sintered at 950°C for 1 h is still mainly perovskite phase but become the tetragonal structure. A few of minor $\text{La}_2\text{Zr}_2\text{O}_7$ phase can be found in the sample, that may due to the generation of the volatile lithium species during sintering. The Y-LLZO sample with Al_2O_3 sintering aid shows higher density and larger grain size after sintering. The thickness of the Y-LLZO coatings are around several μm . The detail electrical properties will be shown in the following report.

Keywords: All solid-state lithium ion battery, LLZO, coatings, colloidal process, solid electrolyte

4:40pm **TS1-2-MoA-10 Technological and Economical Aspects of Precious Metal Sputtering on Full-Size PEM Electrolyzer Components**, *Alexander Wemme (wemme.alexander@vonardenne.com)*, R. Stock, VON ARDENNE GmbH, Germany; C. Simons, Materion Advanced Materials, Germany; S. Kennedy, Materion Corporation, USA

Sputter coating is a well-established process to produce thin layers with excellent properties, which can be used to replace electroplating of electrolyzer components with far less material consumption, hence minimizing cost of coating and thus the overall cost of the electrolyzer stack.

With precious metal material prices constituting up to 98% of the operating cost of a sputter coating equipment, the focus of production control shifts from minimizing downtimes and maximizing output to mitigate material losses as well as possible. Coating operations and the sputter target supply chain have to be evaluated under completely different aspects.

MATERION and VON ARDENNE have cooperated in implementing processes and technologies to drive this paradigm shift in cost structure by developing full-scale rotatable precious metal sputter targets.

The development of precious metal rotary targets will play a dominant role to achieve high utilization of target material thus keeping precious metal input and finance at low level in comparison to planar targets. The focus was to establish a target manufacturing process specifically designed for precious metals offering high homogeneity of target material, perfect sputtering behavior and layer formation. An additional objective was to maximize precious metal utilization by implementing an efficient recycling process.

In this presentation, the results of this recent work to make sputtering of precious metals economically advantageous will be discussed. Additionally, the practical implementation of such sputter targets in coating tools with hardware specifically designed to complement the precious metal life cycle from target fabrication over coatings at industrial scale to recycling is presented.

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