JOINT RISM SEMINAR

On Fast Charge Storage Materials

Co-organized by
CIRIMAT
GIR-TUAT
and RISM

June 14th, 2022
8AM to 10AM (CEST)
3PM to 5PM (JST)

ZOOM

Program

Professor P. Simon
8AM to 9AM(CEST)
3PM to 4PM(JST)

Electrochemistry at the nanoscale: application to materials for energy storage

Dr. E. Iwama
9AM to 9:30AM(CEST)
4PM to 4:30PM(JST)

Materials Transformation : From Battery to Pseudocapacitive Materials for High Energy and High Power Asymmetric Capacitors

Professor W. Sugimoto
9:30AM to 10AM(CEST)
4:30PM to 5PM(JST)

Fast charging TiO_2(B) nanosheets: capacitive versus pseudo-capacitive contribution of size regulated nanosheets

RISM, Shinshu University
risminfo@Shinshu-u.ac.jp

Electrochemistry At The Nanoscale: Application To Materials For Energy Storage

Professor Patrice Simon

UNIVERSITÉ TOULOUSE III – PAUL SABATIER, TOULOUSE, FRANCE

We will show how the confinement of the electrolyte into 3 or 2-dimmensionnal electrode materials affects the ion fluxes and adsorption / charge transfer mechanisms, offering new opportunities to tune the electrode reactivity and reaction kinetics.
Starting with nanostructured carbons, we will show how the combination of several techniques can help for studying the ion confinement effect in carbon nanopores and the associated charge storage increase [1,2]. Moving from double layer to battery-like redox materials, we will show and present how the control of the electrodes structure can help in preparing electrodes with high capacity and high charge / discharge rate using 2-Dimensional MXene materials in non-aqueous electrolytes [3,4].
Finally, we suggest that understanding of electrosorption under confinement in porous and layered materials that results in improved electrochemical performance could be explained by the electrolyte ion partial desolvation observed when confined in nanopores (porous carbons) or in interlayer spacing (2D materials) [6]. Understanding confined electrochemical systems and coupling between chemical, electrochemical, and transport processes in confinement may open tremendous opportunities for energy applications in the future.

References

[1] P. Simon and Y. Gogotsi, Nature Materials 19 (11), (2020) 1151-11633
[2] Y.-C. Wu, J. Ye, G. Jiang, K. Ni, N. Shu, P.-L. Taberna, Y. Zhu and P. Simon, Ang. Chemie 60, 24 (2021) 13317-13322.
[3] B. Anasori et al., Nature Reviews Materials, vol. 2, no. 2, 2017, pp17.
[4] X. Wang, et al., Nature Energy 4, 241–248 (2019)
[5] Y. Li et al., Nature Materials (2020), 19, (2020) 894–899
[6] S. Fleischmann et al., Nature Energy 2022.

Prof. Patrice Simon is Distinguished Professor of Material Science at the Université Paul Sabatier. His research covers the synthesis and characterization of nanostructured materials for electrochemical energy storage sources, including electrochemical capacitors and Li-ion batteries. He is a specialist of interfacial electrochemistry and is more specifically interested in modification of the material/ electrolyte interface for improving kinetics of ion adsorption and charge transfer in electrodes for energy storage applications. Prof. Simon is Deputy Director of the French network on Electrochemical Energy Storage (RS2E, www.energie-rs2e.com) and former director of the Alistore European Research Institute (www.alistore.eu).

He received several awards for his scientific contribution including grants from the European Research Council (Advanced Grant 2012, Synergy Grant 2020), the Horizon Prize from the Royal Society of Chemistry (2021), Conway Prize in Electrochemistry from ISE (2018). He was a Fellow of the International Society of Electrochemistry (2017).
He is a member of the French Academy of Sciences (2019), the European Academy of Sciences (2020), the French Academy of Technologies (2018), and Senior Member of the Institut Universitaire de France (2017).

Materials Transformation : From Battery To Pseudocapacitive Materials For High Energy And High Power Asymmetric Capacitors

Associate Professor Etsuro Iwama

DEPARTMENT OF APPLIED CHEMISTRY,
ADVANCED CAPACITOR RESEARCH CENTER
TOKYO UNIVERSITY OF AGRICULTURE AND TECHNOLOGY

Designing asymmetric supercapacitors, by combining an activated carbon capacitive electrode together with a large-capacity faradaic (battery-like) electrode, is one strategy for further improving the energy-density performance of supercapacitors, thus expanding their applicability. Here, we introduce examples of materials transformation from typical battery to pseudocapacitive electrode materials [1-3] by using different methods such as nanomaterial designing, mechanochemical process, and heteroatomic substitution.

In the presentation, Li_3VO_4 (LVO) will be presented as an example of pseudocapacitive materials transformation. The orthorhombic β-Li_3VO_4 (β-LVO) has been identified as a promising negative electrode material, with theoretical specific capacity of 394 mAh g^{-1} (2 lithium accommodation) operating at a safe but still low potential range between 0.4 and 1.3 *vs*. Li/Li^+ [2]. Recent our studies unveiled that cation-disordered LVO can be electrochemically obtained from the pristine cation-ordered LVO during initial cycling, which we termed as electrochemical activation process [2-3]. This electrochemical activation process induces the transformation of β-LVO from the pristine cation-ordered structure into an activated LVO, which has a Li^+/V^{5+} cation-disordered structure. Charge discharge curves also change from battery-like plateau to pseudocapacitive slope *via* such cation-disordering of LVO, along with its reaction mechanism change from two-phase to solid-solution reaction [2]. Yet, the preparation method of cation-disordered LVO has been a major issue as the electrochemical activation process is impractical from the industrial point of view. Such electrochemical process requires a precycling of β-LVO, which is difficult to control and inevitably produces undesirable irreversible capacity for a full cell assembling.

In this talk, we introduce two alternative processes, mechanochemical ball milling of LVO and heteroatomic substitution of vanadium in LVO, as a direct synthesis method of pseudocapacitive LVO materials.

References

[1] K. Naoi *et al*., *Energy Environ. Sci*., 9, 2143-2152 (2016).
[2] E. Iwama *et al*., *ACS Nano*, **10**(5) 5398 (2016).
[3] P. Rozier *et al.*, *Chem. Mater.*, **30**(15), 4926 (2018).

Dr. Etsuro Iwama has been an associate professor of applied chemistry at Tokyo University of Agriculture and Technology (TUAT) since 2019. He received PhD degree in 2010 from TUAT and was post-doc. researcher in Prof. Patrice Simon's group at CIRIMAT Toulouse (2010-2013). Then, he returned to TUAT to work as an assistant professor (2013-), and then associate professor (2019-). His research focuses on nanomaterials design for next generation supercapacitors / batteries, and materials transformation/collection via electrochemical method for carbon neutrality.
His hobbies are learning foreign languages, hooping, and Arsenal.

PROFESSIONAL EXPERIENCE

2019~ :Associate Professor at Department of Applied Chemistry, TUAT
2014-2019 :Assistant Professor at Department of Applied Chemistry, TUAT
2013-2014 :Project Assistant Professor at Department of Applied Chemistry, TUAT
2010-2013 :Post-doc researcher at Université Paul Sabatier (Toulouse, France)

PUBLICATIONS

(35 Papers and 4 Books Chapters)

1. E. Iwama, N. Kawabata, N. Nishio, K. Kisu, J. Miyamoto, W. Naoi, P. Rozier, P. Simon and K. Naoi, "Enhanced Electrochemical Performance of Ultracentrifugation-Derived nc-Li3VO4/MWCNT Composites for Hybrid Supercapacitors", ACS Nano, 10, 5398-5404, (2016).
2. E. Iwama, P.L. Taberna, P. Azais, L. Bregnon, P. Simon, "Characterization of commercial supercapacitors for low temperature applications", Journal of Power Sources, 219, 235-239 (2012).
3. E. Iwama, F. Shimodate, Y. Oki and K. Naoi, "Super-Enhanced Lithium-ion Transport by an Effective Shift of Solvation Shell Structure in Branched Hydrofluoroether Electrolyte", Electrochemistry, 78, 266-272 (2010).

Fast Charging TiO_2(B) Nanosheets: Capacitive Versus Pseudo-capacitive Contribution Of Size Regulated Nanosheets

Professor Wataru Sugimoto
RESEARCH INITIATIVE FOR SUPRA-MATERIALS,
FACULTY OF TEXTILE SCIENCE AND TECHNOLOGY,
SHINSHU UNIVERSITY

TiO_2(B) is a promising anode for high-rate lithium-ion capacitors and Li-ion batteries. The size and porosity of TiO_2(B) are important factors for high power performance. We have prepared TiO_2(B) nanosheets (ns) with equivalent diameter (*De*) of 300nm and 30nm and manipulated the orientation of the TiO_2(B)-ns by altering the deposition method and drying process. For TiO_2(B)-ns with *De*=300nm, the orientation effect was not clear and the amount of lithiation (SOC) was almost the same and only 20% SOC could be obtained at 0.2C rate. By downsizing to *De*=30 nm, a two times increase in rate performance was obtained for vertically aligned electrodes. Although the orientation of small-sized TiO_2(B)-ns had a large influence on Li^+ transfer kinetics, 100% SOC could not be achieved, suggesting the lack of electronic conductivity. The lack of electronic conductivity could be avoided by adopting a vertically aligned reduced graphene oxide (V-rGO) electrode as a porous current collector. 100% SOC was obtained for TiO_2(B)-ns/V-rGO with *De*=70 and 150nm at 0.5mV/s. On the other hand, only 55% SOC was achieved for nanosheets with *De*=300nm. The trend in Li^+ transfer kinetics becomes clearer at higher scan rate with the capacity scaling with decreasing equivalent diameter.

Prof. Wataru Sugimoto has been a professor of Materials and Chemical Engineering at Shinshu University (Japan) since 2013. He also holds a position as Deputy Director of RISM (Research Initiative for Supra-Materials). He received his PhD degree in 1999 from Waseda University and has been a faculty member of Shinshu University since then. His research focuses on nanomaterials for electrochemical charge storage and conversion. Prof. Sugimoto has received particular recognition for the synthesis and application of conductive nanosheets (RuO_2, IrO_2, graphene, etc.) targeted towards electrochemical capacitors and fuel cells. He has been responsible for several research projects from JST and NEDO, including a JST-ALCA project based on the development of 4V aqueous hybrid supercapacitors.
Prof. Sugimoto has received severa awards including the Oronzio De Nora Foundation Prize of ISE on Electrochemical Energy Conversion in 2005, the 2004 Young Researcher Award (Sano Prize) and the 2018 Scientific Achievement Award of the Electrochemical Society of Japan.

Selected Publications

1. R. Saito, et al. Enhancement in the Charge-Transfer Kinetics of Pseudocapacitive Iridium-Doped Layered Manganese Oxide, *Inorg. Chem*., 61(11), 4566 (2022).
2. T Yoshida, et al. Size Dependent Fast Li Ion Storage Based on Size Regulated TiO_2(B) Nanosheet Electrodes with Vertica Horizontal and Random Alignment, *Electrochemistry*, 88(4), 305-309 (2020).
3. D. Mochizuki, et al. Vertically Aligned Reduced Graphite Oxide Nanosheet Film and its Application in High-Speed Charge/Discharge Electrochemical Capacitor, *ACS Appl. Energy Mater*., 2(2), 1033-1039 (2019).