

## ナノ構造エネルギー変換貯蔵デバイスの非平衡電気化学プロセッシング

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### **Non-equilibrium Electrochemical Processing of Nano-structured Energy Conversion & Storage Devices**

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**ABSTRACT:** “Electrochemical Nucleation & Growth” ESA ITT (PI: Prof. M. Rosso) started the activity in 2010. The team covers 4 categories: 1)Electrochemical Nucleation, 2)Dendritic Growth Process, 3)Kinetic Monte Carlo Simulation and 4)Gas Evolution Electrode. JAXA Nanomaterials WG is going to engage in Electrochemical Processing of Nanostructured Semiconductor Devices in order to support ESA research team. Electrochemical nucleation phenomena of metals are examined with micro- or even nano-capillary electrode fabricated by anodic oxidation process. We have focused ZnO Nanowire Formation Mechanism. Present interest also extends to Electrochemical Processing of Si Nanowire in Ionic Liquid and High Temperature Molten Salt. Amorphous SiO<sub>2</sub> powder refined from diatomaceous earth (5N in purity, DE-SiO<sub>2</sub>) was electrolytically reduced to Si at 1.00 and 1.20 V vs. Ca<sup>2+</sup>/Ca in molten CaCl<sub>2</sub> at 1123 K. Electrochemical processing of Si micro- or nano-rod is now challenged as well as Li electrodeposition in ionic liquids.

Key words: Direct electrolytic reduction, Amorphous SiO<sub>2</sub> powder, Diatomaceous earth, Molten salts, Low-cost Si production, Si & Li electrodeposition, Ionic Liquid, ZnO nanowire

### **Topical Team Meeting Summary**

M. Rosso’s proposal to European Space Agency (ESA) in order to organize the collaboration research on “Gravitational Effects on Non-equilibrium Electrochemical Processing of Nano-structured Energy Conversion & Storage Devices” has been accepted. Following the Kick-off meeting in CNRS (Paris) in Oct. 2009, ESA-ITT meeting was held on Feb. 2<sup>nd</sup>, 2010, (9:30-17:00, Paris). The participants include O. Minster and S. Mazzoni(ESA); M. Rosso, E. Chassing, Ph. Mandin (CNRS), O. Magnussen (Kiel), W. Schwarzacher (Bristol), R. Alkire(UIUC) and Y. Fukunaka (JAXA). After Ph. Mandin was asked to

work as a general secretary, O. Minster gave his introductory talk to regard the present team as ESA ITT team, because of the creation of scientific frontier and future feedback to the industrial technology, especially in the field of environmental and energy.

Y. Fukunaka (JAXA & Waseda Univ.), first of all, introduced his group research achievements on the effects of gravitational level on electrochemical interfacial phenomena mainly done with JAMIC Drop Tower to all participants. Smaller nucleation rate was confirmed to result in longer and more uniformly grown dendrite arm lengths under micro-gravity field. Water electrolysis experiments demonstrated more

visible effects in KOH solution than in H<sub>2</sub>SO<sub>4</sub> solution. Then, he described the secondary battery reversibility guaranteed by the realization of flat electrode surface during repetition of charging and discharging operations. No paper has been however reported on the gravitational effects on the electrochemical interfacial phenomena even in JPL. An application oriented attitude to mainly focus better performance and longer durability is typical characteristics, because of severe competition in EV.

ISS research proposal was additionally introduced based on the analytical cell and observatory cell with SCOF interferometry technique. The competition rate between metal cluster surface diffusion rate and precipitation rate was calculated by a simplified Monte-calro simulation. The dendritic growth phenomena of Cu (or Ag) from CuSO<sub>4</sub> (or AgNO<sub>3</sub>) aqueous solution system as well as Li and Si from PC or ionic liquid system are focused on as well as semiconductor ZnO (ZnNO<sub>3</sub>-LiNO<sub>3</sub> aqueous solution system) and Si (Ionic Liquid) nanowire growth confined in nanospace. The concept of ISS electrochemical laboratory was emphasized with nanostructural materials tailoring in energy conversion and storage devices. He also introduced the works by S. Kjelstrup(NTNU) and D. R. Sadoway(MIT).

R. Alkire (UIUC) then proposed the numerical simulation of electrochemical nucleation and growth processes embedded in multmultiscale simulations codes. He will (1) develop a fast atomic scale KMC algorithm for use in electrochemical nucleation; (2) provide ability to include multiple chemical systems in the algorithm (e.g., Cu, Ag, Zn Systems); (3) make the code user friendly so that experimentalists can make changes to the input on their own; and (4) provide links between the KMC code and a continuum mass transport code such as Kawai and Fukunaka code (2009, 2010).

O. Magnussen (Kiel) introduced the research projects on nanoscale studies of electrified interfaces and electrodeposition processes by scanning tunneling microscopy and surface X-ray diffraction techniques using synchrotron radiation. He and W. Schwarzacher aim at understanding the nucleation and growth processes and the interplay of atomic scale interface structure and electrochemical reactivity. His technique can be applicable to examine the reconstruction of metal substrate surface accompanying H<sup>+</sup> ion reduction. The O<sub>2</sub> evolution phenomena may be challenged.

Ph. Mandin (CNRS) introduced the design concept of gaseous electrode important in the industrial electrolysis.

M. Rosso (Ecole Polytechnique, Paris) and E. Chassaing (CNRS) have been working on the electrochemical dendritic formation. These studies comprise different aspects: numerical calculation and experiments performed on lithium electrodes and other metals like Cu, Ag and Zn. The idea was on the one hand to better understand the interplay between the formation of a passivation layer on lithium electrode surface and the onset of dendritic growth: on the other hand to test quantitatively a model proposed by JN Chazaviel to explain the formation of an irregular deposit on the surface of electrode. This model predicts the formation of non-classical space charge in the vicinity of electrode. It has never been verified experimentally, because of an instability caused by natural convection.

In ECS Spring Meeting in Vancouver (May, 2010) and GRC (Aug. 2010),  $\mu$ -pipetto electrode concept was discussed with Prof. T. Homma (Waseda University, Tokyo). He promised to contribute this project to supply such a micro-pipetto to O.

Magnussen (Kiel). After these discussions, we have determined the following 4 research topics in ESA ITT Meeting held in Nice, Oct. 1<sup>st</sup>, 2010.

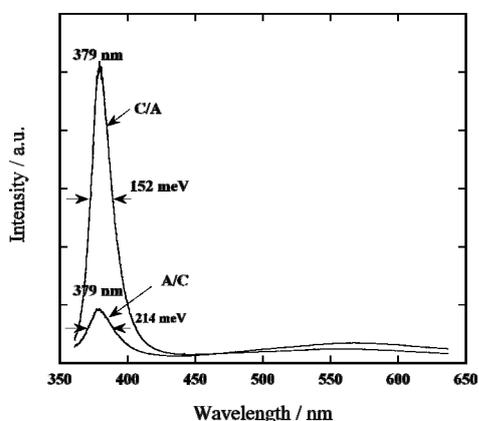
(1) Nucleation of Metal in Micropipet(Ag, Cu?)---O. Magnussen, T. Jacob, Natasha, T. Homma and Y.F.

(2)Dendritic Growth(Ag, Cu, (Li in IL in future))---M.Rosso, E. Chassaing, K. Nishikawa, Y. Sone and Y. F.

(3)Gas Bubble Electrode---Ph. Mandin and H. Matsushima

(4)Multi-scale Modeling---R. Alkire, T. Jacob, C. Miranda & Y.F.

Next meeting is scheduled in ECS Montreal (May), ISPS(July) and ISE(September) in 2011.



**Figure 1.** PL spectra from ZnO nanowire arrays electrodeposited in aqueous solution.

### Non-equilibrium Electrochemical Processing of Nanostructure Energy Conversion & Storage Devices

Free standing ZnO nanowire array was successfully electrodeposited on ITO/FTO substrate by template-free method in  $Zn(NO_3)_2$  aqueous solutions in two different electrode configurations of (C/A) and

(A/C). PL characteristics are measured at randomly selected locations in the deposited array sample. Fig. 1 shows the room temperature PL spectra for  $Zn(NO_3)_2 = 1$  mM. The intensity of UV peaks and  $I_{UV}/I_{GY}$  is higher and FWHM is smaller in C/A configuration. It was also found that more uniform film is obtained in C/A. A kind of natural convection is induced in A/C configuration. The fluctuating concentration of chemical species may disturb the crystallization process of ZnO nanowire.

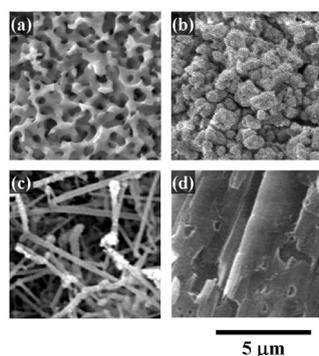
### Future Research Direction in JAXA

Green energy technology must be supported by a possible materials tailoring technology to guarantee the huge production rate of Si solar cell backed up by stable and low cost supply system of natural resources. We have proposed a new electrochemical processing route stemming from the purification of diatomaceous earth. The refined  $SiO_2$  was electrolytically reduced to Si in  $CaCl_2$  melt at 1123K (Fig. 2).

A possible way to electrodeposit Si has been studied in trimethyl-*n*-hexylammonium bis(trifluoromethylsulfonyl)imide containing  $0.1 \text{ mol L}^{-1}$   $SiCl_4$ . Cyclic voltammetry suggests that  $SiCl_4$  should be reduced to form Si around  $-2.0$  V. Potentiostatic electrolysis at this potential forms a yellowish-brown film on a Ni substrate. X-ray photoelectron spectroscopy and Raman spectroscopy reveal that the electrodeposited film contains amorphous Si. It is also found from SEM observation and EDS analysis that highly uniform and dense thin film can be obtained in the initial stage of electrodeposition and that the electrodeposited Si film becomes rougher and thicker with the progress of electrolysis.

The gravitational level may affect the coupling phenomena between the ionic mass transfer rates in electrolyte confined inside meso or nano scale space. In this project, the electrochemical processing of Si

nanowire is now focused in Kyoto University (high temperature molten salt electrolysis) and Waseda University (ionic liquid).



**Figure 2.** SEM images of pellets before and after the electrolysis at 1.00 V for 10 minutes in molten  $\text{CaCl}_2$  at 1123 K. (a) Original DE-SiO<sub>2</sub>, (b) original fumed-SiO<sub>2</sub>, (c) electrolyzed DE-SiO<sub>2</sub>, and (d) electrolyzed fumed-SiO<sub>2</sub>.