# 充放電操作と固液界面現象
# 解説記事---Cu 電極対称セルによるモデル研究(JAMIC 実験)

本間敬之 [1), 福中康博 [2), 國本雅宏 [2), ヴォダルツ・ジギー[1)

1)早稲田大学先進理工学部応用化学科, 2)早稲田大学ナノライフ創新研究機構

# Review Article---Gravitational Effects to Electrochemical Interfacial Phenomena during Charging/Discharging Operation-----Modeling Study with Cu-Electrodes Symmetry Cell-----

*Takayuki Homma, Yasuhiro Fukunaka, Masahiro Kunimoto, Siggi Wodarz*

*Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555

E-Mail: y.fukunaka@kurenai.waseda.jp

Abstract: Charging reaction essentially accompanies the electrodeposition of $Li^+$ ion and Discharge does to electrochemical dissolution of Li metal to electrolyte, when SEI formation can be daringly neglected for Li metal NE in Ionic Liquid. Based on such a presumption, the gravity level effects on the coupling behavior during C/D operation was tried to simulate by the electrochemical reactions Cu in aqueous solution confined in meso-/micro-space at extremely high current density inside JAMIC drop tower. Cu dendritic growth in $Cu^{2+}$ depleted zone during charging operation as well as passive $CuSO_4$ precipitation in supersaturated $Cu^{2+}$ electrolyte zone during discharging could be easily monitored by measuring the electrode potential variations. Induction of a kind convection surely determined the incubation period for the phase transformation phenomena. These results may provide a base toward the multi-scale physical modeling during C/D operation for advanced battery.

*Key words; Physical Model, Charge/Discharge Operation, Battery, Electrodeposition and Dissolution, Coupling Phenomena, Gravitational Level Effect, Review Article*

**1. Introduction**

NASA's major interest was shifted from Lunar Exploration to Mars after Apollo Projects. New York Times HP[1)] wrote "Can the U.S. Really Get Astronauts to Mars by 2030?" on Oct. 12th, 2016, referring President Obama's essay: "We have set a clear goal vital to the next chapter of America's story in space: sending humans to Mars by the 2030s and returning them safely to earth, with the ultimate ambition to one day remain there for an extended time." Additionally, White House and NASA officials announced NASA initiatives that built on the President's vision and utilize public-private partnerships to enable humans to live and work in space "in a sustainable way".

More recently, SpaceX successfully launched its first Falcon Heavy booster in order to demonstrate to be able to send the Tesla's symbolic payload (Elon Musk's Tesla Roadster and a mannequin named "Starman") on a deep-space ride toward the asteroid belt at KSC on Feb. 6, 2018[2)]. The boosters are designed to be reusable. Tesla Roadster is power-trained by Panasonic Battery Assemble. The EV is challengingly designed at 2.1 s to accelerate to 100km/h, maximum speed of 400 km/h and 1000 km as cruising range. The company is also famous to commercialize a home battery system to store the electricity converted from Solar Energy. As seen in these HP articles, the advanced energy conversion and storage technology indispensably becomes a key technology not only in Space Engineering but also to link the renewable energy with the large scale terrestrial Electrical Network in order to establish the Sustainable Society as the President mentioned.

By the way, the advanced battery is characterized by the following aspects as larger energy density, higher output density, longer duration and safety. The first two items are primarily determined by the selection of material chemistry, while the other two strongly depends on Charging/Discharging Operation under a particular environment. It has been frequently pointed out that the battery durability and safety are governed by the smoothness or flatness of electrolyte/electrode interface, especially by irregular morphology of dendritic growth on metal-anode surface during repetition of C/D operations. Many kinds of metal anode have been employed in Space Engineering field since Vanguard (1956) and Спутник-1 (1957). Most missions are successfully conducted as long as the energy conversion and strage devices concern, although Boeing 787 encountered the troubles of smoking or even firing in Li ion battery (LIB) assembles. No fundamental research on *the Gravitational Level Effects* *on the Electrochemical Interfacial Phenomena during C/D Operations* has not been motivated even in JPL. The coupling phenomena between micro-morphological variations and ionic mass transfer confined even in such a meso-space among active electrode materials particles must be understood. Now that, NASA Battery Workshop shows their interests in this subject because the future journey toward Mars based on lunar base necessitates more advanced and safer energy storage devices.

LIB was commercialized in Japan. It is composed of transition metal oxide particles as positive electrode, finer active graphite powder as negative electrode, polymer separator, organic electrolyte with $Li^+$ ion and metal current collector. The adoption of active graphite particle well avoids Li dendrite formation by inducing Li intercalation function, but the cell capacity almost saturates to the theoretical value. New candidate to further increase the capacity is to utilize Li metal NE without dendrite formation. However, Solid Electrolyte Interface (SEI) formation at electrolyte/electrode interface accompanying C/D reactions inevitably introduces the complexity to the Li metal dendrite formation on anode.

Charging reaction essentially refers to the electrodeposition of $Li^+$ ion and Discharge does to electrochemical dissolution of Li metal to electrolyte, when simplified into electrolytic system as imagined from “Physical Chemistry” by P. W. Atkins. The suppression of Li dendrite growth is a dream for energy researchers. Many players are engaging in in-situ diagnostics and physical modeling. Thus, it is decided not to touch Li chemistry accompanying a complicated side reaction of SEI formation but to considerably simplify the electrochemical reaction in aqueous solution. That is, the electrodeposition and electrochemical dissolution of Cu in $CuSO_4$ (aq.) under microgravity is focused to understand the gravitational effects to C/D operation on metal anode.

## 2. Gravitational Level Effects on Coupling Phenomena

Coupling Phenomena between Morphological Variations and Ionic Mass Transfer Rate is typically demonstrated in a quasi-2D electrolytic cell with 200 μm thick electrolyte layer (Fig. 1). Electrodeposited Cu dendrite radially grows on a periphery of 100 μm thick Cu cathode disc installed horizontally, while does anisotropically in a vertical cell within 90 seconds (Fig. 2). The only difference is the cell configuration between horizontal and vertical. Lighter electrolyte near Cu disk cathode introduces a kind of natural convection even in such a narrow space of 200 μm electrolyte layer to result in a morphological change due to the coupling phenomena.

## 3. Experimental Design on Fundamental Aspects of C/D Operation[3-6)]

Electrochemical Interfacial Phenomena accompanying C/D operation on Li metal NE in ionic liquid (future candidate of NE for advanced battery) may be daringly modeled as the electrodeposition of $Cu^{2+}$ and electrochemical-dissolution of Cu anode in $CuSO_4$ (aq.) solution. That is, Cu-Electrodes Symmetry Cell is designed similarly to M. Rosso[7-10)] in order to understand the gravitational level effects on the coupling phenomena during C/D operation of metal NE battery. Quasi 2D Electrolytic Cell with annular Cu-electrodes was set in JAMIC Exp. with Common Path Interferometer. Extremely high current density has to unfortunately apply to visualize the morphological variations within 8 to 10 sec in a dropshaft, which is a biggest weak point for the present purpose. The results are compared with those conducted in terrestrial experiments.

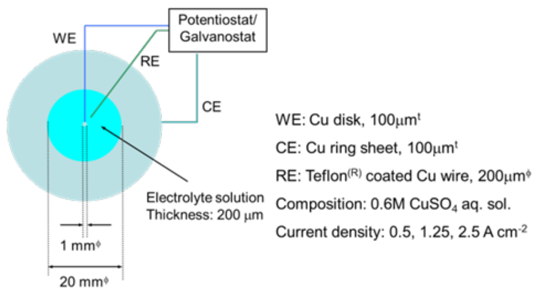

Fig.1 Schematic illustration of quasi-two dimensional electrolytic cell.

Fig.2 Morphological variations of electrodeposited copper; $G$=1 G; $i$=2.5 A cm$^{-2}$

## 4. Results and Discussions

### 4-a. Electrodeposition[3)]

Less Nucleation on Cu Substrate was observed in

SEM for galvanostatic electrodeposition. That is, Fig. 3 illustrates clearly longer and more uniform dendrite growth corresponding to a quick increase of concentration overpotential around 4 sec under μ-G in Fig. 4. Transient diffusion model with migration effect predicts substantially zero $Cu^{2+}$ concentration at 3sec after starting the electrolysis.

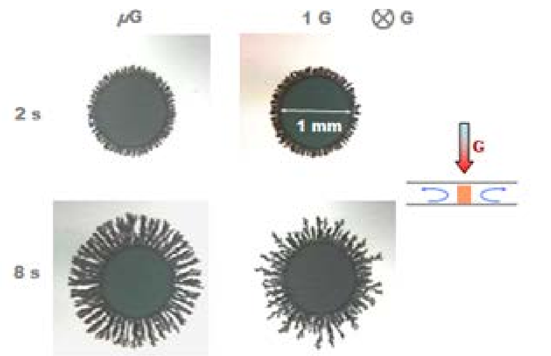


Fig.3 Morphological variations of electrodeposited copper; $i$=2.5 A $cm^{-2}$

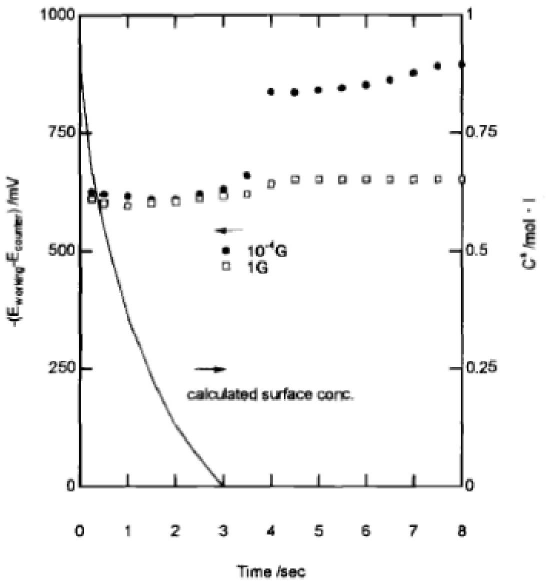


Fig.4 Time variation of potential difference (0.9 M $CuSO_4$, 0.3 A $cm^{-2}$), (after Ref. 3)

**4-b. Anodic Dissolution[4)]**

Now, the polarity is reversed in quasi 2D cell. Cu disk anode was galvanostatically dissolved in 0.1M$CuSO_4$-1.1M$H_2SO_4$ solution. Fig. 5 compares the transient variations of anodic overpotential at various current densities in μ-G with those in 1-G. The anodic overpotential gradually continues to rise with time above 0.8 A/$cm^2$ in 1-G, while it starts to quickly increase around 6 sec in μ-G. Such a tendency is more enhanced at 1.4 A/$cm^2$ and an overpotential jump appears even in 1-G. Anode surface characterization with XPS and Holographic Interferometry observation with more precise optical arrangement certainly demonstrates this overpotential rise caused by anodic passivation due to $CuSO_4$ nucleation or precipitation after an incubation period in supersaturated aqueous electrolyte zone adjacent to anode.

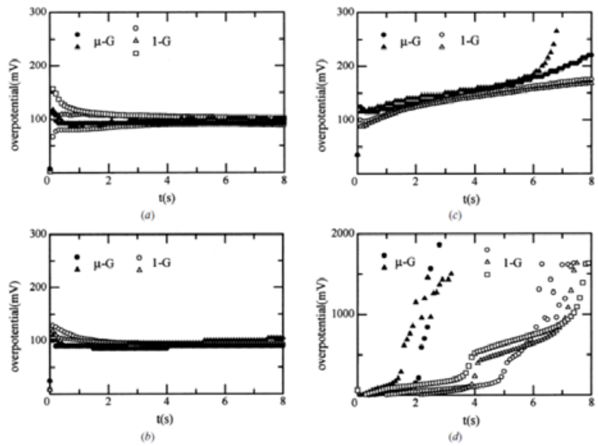


Fig. 5 Time variation of anodic overpotential (effect of current density): (a) $i$=0.2 A cm-2, $iR$= 53 mV; (b) $i$ =0.5 A cm-2, $iR$ = 130 mV; (c) $i$ =0.8 A cm-2, $iR$ = 210 mV; (d) $i$ =1.4 A cm-2, $iR$ = 370 mV (after Ref. 4)

**5. Summary**

C/D operation of Li metal NE may be modeled without SEI formation phenomena by employing Cu electrodes symmetry cell. JAMIC Drop Tower experiments were originally conducted in order to demonstrate the interesting electrochemical interfacial phenomena encountered in electrochemical machining or microelectronics fabrication[3,4)]. Fortunately, these data may be regarded also for C/D operation for a model battery with Cu symmetry electrodes excluding the applied extremely high current density characteristics of short μ-G duration less than 10 seconds. Moreover, the coupling phenomena is surely governed by the electrochemical nucleation and growth process at electrolyte/electrode interface confined inside meso-space, even under such a microgravity circumstance at lower current density and over corresponding longer duration over $10^3$-$10^8$sec(nearly 3 years). The present model may provide a good starting point to construct a multi-scale physical model of advanced battery for space engineering applications.

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