

# 電気化学反応に伴う金属電極表面形態変化と物質移動速度の連結現象と重力レベル効果

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## Gravitational Level Effects on Coupling Phenomena between Morphological Variations of Electrode Surface and Ionic Mass Transfer Rate

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**Abstract:** Horizontally upward-facing Zn anode surfaces combined with Ni(OH)<sub>2</sub>/NiOOH cathodes in 1.95M KOH aqueous solution were electrochemically dissolved and deposited with pulsed current. The morphological variations of Zn hydroxide precipitates on the Zn anode surface were also examined as a function of two pulse width at three different locations on the anode surface with the ex-situ SEM observation. It was different from the size of many hexagonal crystals of zinc oxide after pulsed current for both period. The present model provides insight to the analysis of observed morphological variations along the Zn anode surface. Such a research may introduce a more profound understanding on Li battery operation in space environment as well.

*Key words:* Energy Conversion & Storage, Coupling Phenomena, Pulse Electrolysis, Dendrite

### 1. Introduction

The year of 2016 celebrates the 60<sup>th</sup> anniversary of the space program that began with the launch of the 1<sup>st</sup> Sputnik in 1956. Thanks to the rapid development on the flexibility and capacity of batteries and fuel cells, tremendous progress has been made in the exploration of space engineering since then. Space missions impose several critical performance requirements on battery and fuel cells. Dr. S. Surampudi (Caltech, JPL researcher) described as follows (Energy & Fuel Cell in Space: Interface, Fall, p.25-30, 1999). "Batteries must be capable of operating in a high vacuum and withstand severe launch environments including vibration, shock and acceleration. Maximum electrical energy in minimum weight and volume must be provided. Long cycle life more than 30,000 cycles is the critical driver for orbiting spacecraft and long active shell life more than 7 to 10 years is the driver for planetary probes. Radiation resistance and operation at temperature as low as -80°C is essential for some planetary missions."

URFC and Li battery are the key devices as well as Life Supporting system in Space Exploration toward to Mars. Electrochemical interfacial phenomena must play the most important role in these devices. Nevertheless, the effect of gravitational level to the electrochemical interfacial phenomena

has not been seriously examined even in JPL because of successful operation of these devices in space environment.

The gravitational level effect to the electrochemical processes like water electrolysis and secondary batteries was examined in JAMIC Drop Tower. Ni-Zn battery was installed on the top of capsule. After dropping the capsule in the shaft, the charging operation of battery was indispensable. It provided us a strong impact how important the energy conversion & storage devices are in the space exploration as demonstrated in the movie, "Apollo the 13th".

Now that, this subject is focused in the field of advanced battery utilization stimulated by Boeing 787 events. More importantly or practically, this trend has been further stimulated by the increased public consciousness on global warming issue. Rechargeable batteries for electric vehicle (EV) and hybrid electric vehicle (HEV) applications have been a subject of intense focus for the last decade or so.

Although Li-based systems have received the most attention, there has been increasing interest in Zn-based systems because of their lower costs, material abundance, and compatibility with nonflammable aqueous electrolytes. Zn anode morphological variations however introduce some serious problems of short life, poor reliability, and safety issues. The

coupling phenomena between ionic mass transfer rates and electrode surface morphological variations must be well understood. The goal is to incorporate the fundamental knowledge of Zn electrochemical processes into a numerical model for a hybrid electric vehicle (HEV) battery as well as large-scale battery operation.

It is of practical importance to predict the cell voltage and current distribution of a battery for vehicle applications with a numerical model, as an aid to the design of an electric control unit (ECU). Therefore, the physical model pore simulation considering only diffusion and electrophoresis mechanisms is described. An electrochemical cell with a horizontal upward-facing Zn anode nearby a plan-parallel Ni(OH)<sub>2</sub>/NiOOH electrode has been used frequently in order to suppress the natural convection induced by buoyancy forces. Pulse modulation operation in order to improve the durability of Zn anode is introduced in the present manuscript. Pulse width was varied in order to confirm the effectiveness.

## 2. Experimentals

The experimental apparatus is drawn in Figure 1. Briefly, an electrochemical cell was fabricated from an acrylic plate, and a 99.99% zinc plate was used as the working electrode. The Ni(OH)<sub>2</sub>/NiOOH counter electrode was charged to 50–80% state of charge before cell discharge. This configuration was adopted to suppress the natural convection driven by buoyancy forces. In the present work, a polyolefin separator is placed between the negative and positive electrodes. The [Zn(OH)<sub>4</sub>]<sup>2-</sup> ions are blocked by the separator surface adjacent to Zn electrode because of the larger size of the [Zn(OH)<sub>4</sub>]<sup>2-</sup> ions compared to OH<sup>-</sup> and K<sup>+</sup> ions. Certainly, such an assumption would not be valid in a practical cell after many cycles or an extended cell charge or discharge, but it should be a good approximation for a short-duration experiment. The tip of a Hg/HgO reference electrode was positioned about 3 mm from the Zn working electrode. Galvanostatic electrolysis was carried out in a 1.95 M KOH (10% by weight KOH) aqueous electrolyte at 293 K. Pulse scheduling is illustrated in Fig. 2. Experimental details should be referred to our papers as well as

the ISAS proceedings published in 2014.

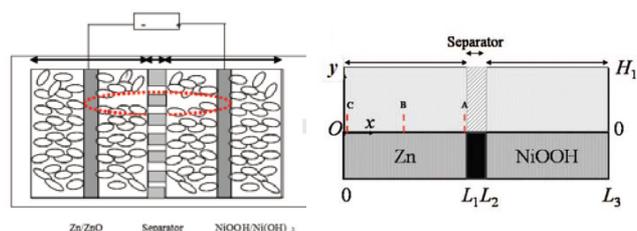


Figure 1

## 3. Results & Discussion

The surface morphological variations of Zn anode were examined. The electrochemical dissolution of the Zn anode was carried out over various periods after starting the galvanostatic electrolysis at the average applied current densities of  $i_{ave} = 20$  and  $40$  mA/cm<sup>2</sup> (HA-305 galvanostat, Hokuto Denko LTD.). The electrolysis duration time was determined with the aid of numerical simulation. Each electrode was freshly prepared before electrochemical testing. The discharged electrode was removed from the electrochemical cell and rinsed with ethanol. Three points on the Zn anode surface were selected for SEM observation: adjacent to the separator, the center of electrode, and near the current collector wire.

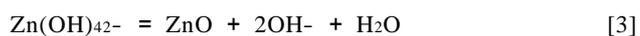
During the discharge of Zn-NiOOH batteries, OH<sup>-</sup> is consumed on the Zn electrode surface, as expressed by [1]

$$\text{Zn} + 4\text{OH}^- = \text{Zn}(\text{OH})_4^{2-} + 2\text{e}^- \quad [1]$$

The electrochemical reaction on NiOOH electrode can be also expressed as follows.



Eq. 1 does not *a priori* involve the dissolution-precipitation mechanism of [Zn(OH)<sub>4</sub>]<sup>2-</sup> ions and ZnO. When the [Zn(OH)<sub>4</sub>]<sup>2-</sup> ions concentration on the anode surface exceeds the chemical solubility limit or the electrochemical solubility limit, the precipitation of ZnO or Zn(OH)<sub>2</sub> may take place, which can be written by the following chemical reaction equation.



The holographic interferometry technique might provide such information at a geometrically flat electrode surface. Once the surface becomes rough with hydroxide precipitation, interferometry may lose the capability to monitor the transient behavior of two-dimensional refractive index profiles disturbed

by the surface roughness as well as by the heterogeneous reactivity at the Zn anode surface along an optical path. Thus, *ex situ* observation of surface morphology for Zn anode is presented and discussed in combination with the numerical simulation in this study.

Transient mass transfer rates of both  $[\text{Zn}(\text{OH})_4]^{2-}$  and  $\text{OH}^-$  ions during discharge operation of Zn-NiOOH cell in a 1.95 M KOH aqueous electrolyte are numerically analyzed. Three regions can be identified: Zn electrode compartment, polyolefin separator compartment, and NiOOH electrode compartment. The governing electrolyte-phase equations in each compartment can be expressed according to mass conservation and electroneutrality equations under the assumption of constant physical properties.

Both anodic and cathodic current density distributions are calculated along the electrode surface. The Zn anode surface overpotential  $\eta_s$  can be expressed according to the Butler-Volmer equation. The anode surface overpotential can be calculated by using the constraint condition that the integration of local current density over the electrode surface area must be equal to the applied constant overall electrolytic current  $I$ . The present numerical model does not consider the electrode shape change due to both the dissolution of Zn and the precipitation of ZnO during electrolysis. Therefore, the electrode surface is assumed to be perfectly flat during the numerical simulation. The above-described 2D mathematical model was solved numerically by using the finite differences method and deterministic relaxation techniques.

Figure 2 shows the pulse scheduling. After a zinc electrode was discharged for  $t=3030$  seconds, it was engaged at  $20\text{mA}/\text{cm}^2$ , pulsed current with a pulse period of  $t=0.1$  and 30 seconds and rest time was also  $t=0.1$  and 30 seconds. Note that total discharge coulomb numbers are  $60.6\text{C}/\text{cm}^2$  at  $t=3030\text{s}$  before pulse operation,  $60.602\text{C}/\text{cm}^2$  and  $61.2\text{C}/\text{cm}^2$  at  $t=0.1\text{s}$  and 30s after pulse operation, respectively. Therefore, we compared the morphology before and after pulse operation as the same coulomb number. As for SEM observation,

electrolysis condition before and after pulse operation is unified just after discharging operation in order to compare with the morphology of Zinc oxide precipitation in the same condition. Three points on the Zn anode surface are selected for SEM observation: just next the separator, the center of the electrode and near that current collector wire as illustrated by the dashed line in Figure 1. The details are shown in our previous work [6].

Many hexagonal crystals are observed on porous network morphology at the electrode surface near separator after a zinc electrode was discharged for  $t=3030$  seconds (Fig.3 (a)). On the other hand, the anode surface is mainly covered with a myriad of smaller particles at  $x=0.1$  and 4 mm (Fig.3 (b), (c)).

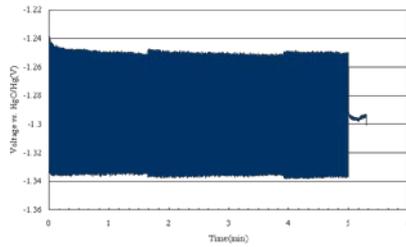
After it is engaged pulsed current with a pulse period of  $t=0.1$  and 30 seconds, many hexagonal crystals at the electrode surface near separator became smaller than that before (Fig.3 (d), (g)). The particle size is 12~15mm before pulse (Fig3 (a)), 1~5mm with a pulse period of  $t=0.1$  seconds (Fig3 (d)) and 5~10mm with a pulse period of  $t=30$  seconds (Fig3 (g)).

A network of hydroxide precipitation near separator was halfway to crumble after pulsed current with a pulse period of  $t=0.1$  seconds (Fig.3 (d)), comparing before pulse operation. On the contrary, a network after pulsed current with a pulse period of  $t=30$  seconds (Fig.3 (d)) remained as same as before. A myriad of small particle formed inside a network at  $x=7.9\text{mm}$  after pulse current with  $t=0.1$  seconds. The number of small particle (about 1mm) in the network with  $t=0.1$  seconds is more than that before pulse.

At  $x=0.1$  and 4 mm, a myriad of smaller particles became more densely packed than that before pulsed current with a pulse period of  $t=0.1$  and 30 seconds. It suggested that the newly formed particles filled in interspaces between particles. Moreover, there was no dendrite growth of zinc with both 0.1 and 30s pulse for about only 300 seconds. It suggests that pulse operation is inhibited dendrite growth. This may

propose long life Ni-Zn battery under optimal pulse condition.

C1:Pulse width=0.1s



C1:Pulse width=30s

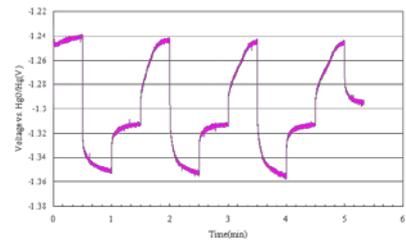


Fig.2 Charge/Discharge curves under pulsed current for 5min at 20mA/cm<sup>2</sup>. Pulse width C1=0.1s(Rest 0.1s), C2=30s(Rest 30s)

Our *ex situ* SEM observation results are now described.

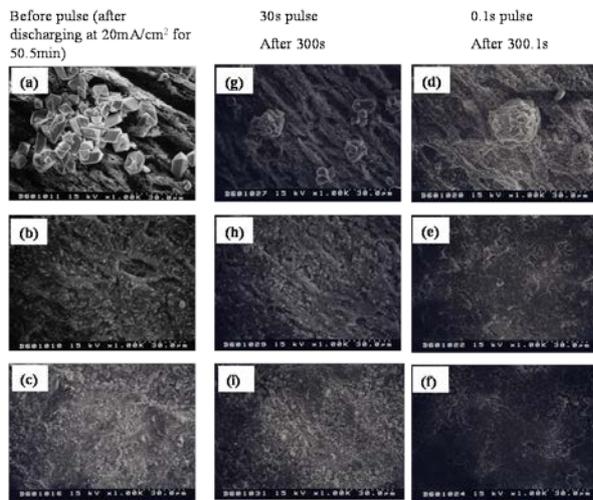


Fig.3 The surface of Zn anode under pulsed current before and after.  
 (a)-(c): Before pulse (after discharging at 20mA/cm<sup>2</sup> for 50.5min)  
 (d)-(f): after 5min minutes by 0.1 seconds pulse at  $i_{ave} = 20\text{mA/cm}^2$   
 (g)-(i): after 5min minutes by 30 seconds pulse at  $i_{ave} = 20\text{mA/cm}^2$   
 (a), (d), (g).  $x=7.9\text{mm}$ , (b), (e), (h).  $x=4\text{mm}$ , (c), (f), (i).  $x=0.1\text{mm}$

Hydroxide is preferentially precipitated at specific active areas. As time progresses, the precursors of quadrangular crystals begin to grow into a film. These spherical particles are initially less than 1  $\mu\text{m}$  in size, and then grow gradually to form rectangular parallelepiped precipitates along the ridge-like lines of polishing scratches. In the early stages of Zn surface oxidation, it is lightly covered with a thin and densely packed layer of many ZnO or Zn(OH)<sub>2</sub> small particles. The OH<sup>-</sup> ion in

the bulk electrolyte easily diffuses to the surface of the Zn electrode from the NiOOH electrode through the separator because the OH<sup>-</sup> ion is very small. Zincate ion also diffuses through the interparticle space in this thin layer. Its calculated surface concentration under the presumption of no ZnO precipitation has exceeded the electrochemical solubility. This layer is thus expected to be an important determinant of battery charging and discharging rates.

A fibrous network or porous morphology of hydroxide precipitation is formed in the next stage. Furthermore, the morphology of the hydroxide precipitate develops a typical quadrangular column at  $t = 15240$  seconds. SEM images clearly demonstrate the appearance of a typical orthorhombic plate crystal layered structure near the separator. Some mossy types of precipitations are also observed between these quadrangular columns.

#### 4. Conclusions

Horizontally upward-facing Zn anode surfaces combined with Ni(OH)<sub>2</sub>/NiOOH cathodes in 1.95M KOH aqueous solution were electrochemically dissolved and deposited with pulsed current. The morphological variations of Zn hydroxide precipitates on the Zn anode surface were also examined as a function of two pulse width at three different locations on the anode surface with the *ex-situ* SEM observation. It was different from the size of many hexagonal crystals of zinc oxide after pulsed current for both periods. Such a methodology may be applied to the dendritic growth process in Li battery as well. ESA-ITT team “Electrochemical Nucleation & Growth”(PI: Prof. M. Rosso, Ecole Polytechnique, 31 participants including 8 countries) has been organized to engage such a project in ISS. Battery safety research in space environment must be developed based on the “Electrochemical Interface Processes for Space Battery and Devices” as WG even in JAXA.