Electrochemical redox reaction of zinc ions at a Ni electrode in ZnCl$_2$-based aqueous solutions

S Jeong
Department of Chemical Engineering, Soonchunhyang University, Asan, Chungnam 31538, Republic of Korea

E-mail: hamin611@sch.ac.kr

Abstract. The electrochemical redox reaction of zinc ions on a nickel electrode was investigated in aqueous solutions containing different concentrations of zinc chloride (ZnCl$_2$). A relatively good cycle efficiency was obtained from the high-concentration solution. The charge and discharge of the nickel electrode exhibited a high cycle efficiency of 92% in the fiftieth cycle in a 2 mol dm$^{-3}$ (M) solution, and a low cycle efficiency of ~43% in the 0.02-M solution. Atomic force microscopy revealed that the dendritic zinc formed on Ni produced different morphologies as the electrolyte concentration increased, resulting in the changes in cycle efficiency. Moreover, the sizes of the zinc particles deposited on the nickel electrode were dependent on the electrolyte concentration. After five cycles, the zinc particles generated in the 0.02-M solution were smaller than those generated in the 2-M solution; however, after fifty cycles, the former particles were larger than the latter.

1. Introduction
Secondary batteries are devices that can be used semi-permanently by using an external power source and repeatedly cause electricity to flow through them in a direction opposite to discharge. Their importance is increasing with recent developments in the mobile communications industry, and they are expected to play a crucial role in the core industries of information, communication, and electronics, along with semiconductors and internet of things. This is because high-performance secondary batteries are expected to accelerate the development of the mobile communications industry. In order to realize high-performance and long-term use of electronic products, it is essential to lower the power consumption of the components and increase the capacity of the power sources. However, there is a limitation on the extent to which the power consumption of a device can be reduced; therefore, much effort has been focused on the development of a secondary battery with a high energy density and a long lifetime.

Since the characteristics of a battery are determined by the anode, cathode, and electrolyte, which are its main components, significant material development is required to improve the performance of a battery. One material that can meet this demand is zinc. It is a non-toxic metal that is abundant and has long been widely used as an anode material for primary cells. Zinc is inexpensive and has good electrochemical capacity (theoretically 820 Ah/kg). In recent years, especially as environmental issues have greatly increased, zinc is attracting more attention as an environmentally friendly material. For this reason, zinc electrodes are most widely used as negatively charged electrode materials for alkaline batteries, including Zn/air and Zn/Ni batteries [1-4].
Although zinc exhibits excellent characteristics as an electrode material in a primary battery, in order to use it as an electrode in a secondary battery, the growth of dendritic zinc on the surface of the electrode caused by repeated charging and discharging must be overcome [5-8]. This dendritic zinc is one of the causes of irreversible loss of capacity of a battery, and when it grows, the lifetime is shortened and safety deteriorates. Therefore, many efforts have been made to suppress the formation of dendritic zinc, but no effective method has yet been found.

There have been extensive studies on dendritic lithium metal produced by the dissolution and deposition of metal ions [9-12]. This is because a lithium secondary battery using the redox reaction of lithium ions as an electrode reaction exhibits excellent performance. Recently, interesting research results have been reported for the dissolution and deposition of lithium. The redox reaction of lithium ions occurring at the interface between graphite (or nickel metal) electrodes and propylene carbonate-based solutions containing lithium salt is greatly influenced by the electrolyte concentration. Even without the use of special additives, changes in the electrolyte concentration significantly change the reaction in the battery. Lithium insertion into graphite does not occur in a low-concentration solution but does occur in a high-concentration solution, and the growth of dendritic lithium on the nickel surface is greatly suppressed in a high-concentration solution.

In this study, the findings obtained from the redox reaction of lithium ions were applied to an electrochemical system using zinc as an electrode. The aim of this study was to understand the effect of zinc ion concentration on the electrochemical redox reaction of zinc by focusing on the concentration of zinc chloride dissolved in the electrolyte solution as a factor affecting the growth of dendritic zinc.

2. Experimental
The charge/discharge measurements and cyclic voltammetry (CV) were performed using a laboratory-made cell, as shown in figure 1. A nickel plate (20 × 20 × 0.5 mm, Nilaco Co.) polished with alumina powder (0.1 μm, Bailkowski International Co.) to a mirror finish was used as the working electrode. Cleanly polished nickel was brought into contact with an electrolyte solution using an O-ring. A platinum mesh and Ag/AgCl (99.99%) were used as the counter and reference electrodes, respectively. The electrolyte solution was prepared by dissolving ZnCl₂ (95%, Junsei Chemical Corp.) in deionized water (HPLC, Burdick and Jackson). The current density for the zinc dissolution and deposition was set to 0.4 mA cm⁻². Zinc was deposited at 0.6 C cm⁻² and dissolved until the potential reached −0.19 V versus Ag/AgCl. CV was conducted between −1.0 and 0.0 V at a sweep rate of 0.5 mV s⁻¹. Atomic force microscopy (AFM) observations were carried out in conventional contact mode using an AFM system (PicoSPM, Molecular Imaging). Pyramidal silicon nitride (Si₃N₄) tips mounted on a triangular micro-fabricated cantilever with a length of 200 μm and a spring constant of 0.02 N m⁻¹ (OMCL-TR400PSA, Olympus) were used for the AFM measurements.

![Figure 1. Three-electrode cell used in electrochemical experiments.](image)
3. Results and discussion
The cycle efficiencies for the electrochemical redox reaction of zinc in the three electrolytic solutions of different concentrations are shown in figure 2. The cycle efficiency is defined as the ratio of electricity used for charging (zinc deposition) to that used for discharging (zinc dissolution) in each cycle. In a 0.02 mol dm$^{-3}$ (M) solution, the variation in efficiency according to the cycle progression was very large and the cycle efficiency decreased sharply after ten cycles, resulting in ~43% cycle efficiency in the fiftieth cycle. In contrast, in the 0.2- and 2-M solutions, the cycle efficiency increased sharply in the initial five cycles, and then was stable up to the fiftieth cycle. In all three electrolyte solutions used, the efficiencies began at a very low value of 40–80% in the first cycle and then increased in the first five cycles. This is probably due to the irreversible consumption of charge during stabilization of the electrode by the film generated on the Ni electrode from the decomposition of the electrolyte solution.

The different electrochemical behaviors of the Ni electrode for the different solutions as described above is presumed to be because the solvation structure of the zinc ions present in the electrolyte is different in each solution. In the electrolyte solution, the zinc ions do not exist alone, but in a solvated state that is weakly bound to the solvent, and the solvation number is known to depend on the concentration of the electrolyte. Therefore, the structure of the solvated zinc ions affects the deposition and dissolution of zinc, which occurs as a result of the electron transfer reaction between the solvated zinc ions and the electrode, which may have caused the difference in efficiency.

The results shown in figure 2 indicate that the electrochemical reaction in the nickel electrode is changing with each cycle. In order to confirm this, the CVs of the electrodes after fifty cycles in the 0.02- and 2-M solutions were measured and the results are shown in figure 3. The redox peaks near −1.0 V due to deposition and dissolution of zinc were observed in the 2-M solution but not in the 0.02-M solution. That is, there is no doubt that the state of the surface of the Ni electrode was changed by the progress of the cycle, and thereby the deposition and dissolution reactions of zinc were affected.
The above cycle efficiency and CV results indicate that the growth of dendritic zinc is highly dependent on the electrolyte concentration. In order to confirm the relationship between the growth of dendritic zinc on the electrode surface and the electrolyte concentration, the surface of the electrode cycled in the 0.02-M solution with poor cycle efficiency and in the 2-M solution with relatively good cycle efficiency was observed using AFM. In order to observe the surface of a sample using AFM, a substrate with a very flat surface is required; the surface of the Ni electrode should be very flat and is therefore sufficient for AFM observations. Figure 4 shows the surface morphology of Ni metal polished using alumina as a substrate used for zinc deposition and dissolution. A linear scratch formed by the alumina during polishing was observed over the entire surface, and it was found that it had sufficient roughness to be observed with AFM.

**Figure 4.** AFM image (5 × 5 μm) of the pristine Ni substrate polished with alumina powder

Figure 5 shows AFM images obtained from the surface of the electrode after five, ten, thirty, and fifty cycles in the 0.02-M electrolyte solution. Scratch marks due to polishing are still observed on the surface of the electrode after five cycles (figure 5(a)), and substances presumed to be dendritic zinc are observed all over the surface. These substances grew to a fairly large size after 30 cycles, with very large variations in size (figure 5(c)). A clear image was not obtained after ten cycles (figure 5(b)), which is believed to be due to the very irregular growth of the dendritic zinc on the surface, resulting in poor surface smoothness. That is, at ten cycles, the growth of dendritic zinc has already begun. This
is consistent with the rapid decrease in cycle efficiency after ten cycles, as shown in figure 2. By thirty cycles, dendritic lithium had grown over the entire surface, and after fifty cycles the flatness of the electrode surface again became very poor, and no clear surface morphology was obtained.

![AFM images](image-url)

**Figure 5.** AFM images (5 × 5 μm) of the Ni electrode in a 0.02-M electrolyte solution after (a) five, (b) ten, (c) thirty, and (d) fifty cycles.

The above AFM results revealed that the growth of dendritic zinc was very rapid in the 0.02-M solution, and progressed very irregularly according to the location of the electrode. Figure 6 shows AFM images of the electrodes in the 2-M solution under the same conditions as figure 5 for comparison. Scratches similar to those observed in the 0.02-M solution were observed on the surface of the electrode after five cycles, as shown in figure 6(a), and particle-like substances were generated on the surface. The larger number of scratches in figure 6(a) than in figure 5(a) after five cycles indicates that a smaller amount of dendritic zinc was formed on the electrode surface in the 2-M solution. That is, it can be considered that the growth of dendritic zinc was suppressed in the 2-M solution. However, after repeated cycles in the 2-M solution, the amount of dendritic zinc increased. After fifty cycles, scratches due to polishing are not observed at all, and the sizes of the particle-like substances deposited on the surface are slightly increased (figures 6(b)–(d)). In addition, the surface of the electrode obtained from the 2-M solution was very flat, and thus relatively clear AFM images could be obtained. From the AFM results shown in figures 5 and 6, it is necessary to uniformly deposit small-sized zinc particles on the electrode surface in order to suppress the growth of dendritic zinc, which is closely related to the electrolyte concentration.

### 4. Conclusions

The electrochemical redox reaction of zinc is strongly influenced by electrolyte concentration. The dendritic zinc produced in 0.02- and 2-M solutions exhibited different shapes in the initial cycles. As
the number of cycles increased, the dendritic zinc in the 2-M solution was maintained without significant changes in shape, while dendritic lithium in a 0.02-M solution has been observed to grow significantly. The effect of electrolyte concentration is presumed to be due to the structural differences in solvated zinc ions. However, from this study, it is unclear what kind of difference this is, and further analysis by Raman spectroscopy is necessary.

![AFM images](image-url)

**Figure 6.** AFM images (5 x 5 μm) of the Ni electrode in the 2-M electrolyte solution after (a) five, (b) ten, (c) thirty, and (d) fifty cycles.

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