

Magnesium Battery Current Collectors for Evaluation of Positive Electrode Active Materials in a Grignard Reagent-Based Electrolyte

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Magnesium (Mg) batteries have attracted significant interest as low-cost batteries with high electromotive force, capacity, and safety. This is partly attributed to the superior property of Mg in having two valence electrons and the lowest standard electrode potential (*ca.* -2.36 V vs. SHE) among the air-stable metals[1]. There is another advantage that Mg metal can be used as a negative electrode material with significantly high capacity (*ca.* 2200 mAh g^{-1} , 3830 mAh cm^{-3}) since a Mg deposit does not tend to form dendrites. Furthermore, Mg resources are abundant and widely spread in the world.

One path to the realization of Mg batteries with such excellent properties was trailblazed by Aurbach et al.², who reported a series of detailed studies of reversible Mg deposition and dissolution in ethereal electrolytes based on the Grignard reagents (RMgX, where R: alkyl or aryl group, X: halogen) in addition to some Chevrel compounds as positive electrode active materials. However, there still remain many issues to be solved for the realization of commercial Mg rechargeable batteries. For example, it is necessary to develop electrolytes with a wider potential window (electrochemically-stable potential region), rechargeable positive electrode active materials with higher redox potentials and charge-discharge rates, and low-cost current collectors.³

We have investigated the current collectors stable at high potentials for the evaluation and discovery of novel positive electrode active materials working in Grignard reagent-based electrolytes.^{4,5} The presence of corrosive halide anions in Grignard reagent-based electrolytes causes the pitting corrosion of affordable metals such as Al, Cu, Ni, Ti, and stainless steel. In contrast, noble metals, glassy carbon, and Nb are stable in the Grignard reagent-based electrolytes. Figure 1 shows cyclic voltammograms measured in the potential range from -1.0 to 4.0 V vs. Mg using the stable working electrodes. The current density for electrolyte oxidative decomposition is different with the kind of electrode, and is the lowest on Nb, resulting in wider potential window of the electrolyte about 3.5 V vs. Mg. Furthermore, the shape of the voltammogram does not change during 10 cycles except for the slight increase in the anodic current density above 3.5 V vs. Mg. Figure 2 shows surface SEM images of Nb after cyclic voltammetry in the potential range from -1.0 to 4.0 or 5.0 V vs. Mg. Both corrosion pittings and deposits are not observed on the Nb surface after the cyclic voltammetry in the potential range from -1.0 to 4.0 V. After the voltammetry in the potential range from -1.0 to 5.0 V, a complicated structure composed of carbon is observed; this could be the product of the electrolyte oxidative decomposition. Thus, it can be concluded that the widening of the potential window on Nb is attributed to a kinetic effect, i.e. lower catalytic activity of Nb for the electrolyte oxidative decomposition

compared with those of Pt and glassy carbon.

Some evaluation examples of positive electrode active materials for Mg batteries will also be presented and its perspective will be discussed in light of our recent development of the stable current collectors.

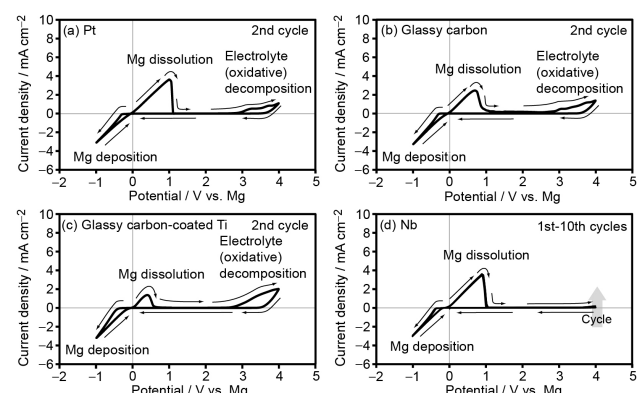


Figure 1. Cyclic voltammograms measured using (a) Pt, (b) glassy carbon, (c) glassy carbon-coated Ti, and (d) Nb electrode in THF solution containing 0.50 M PhMgCl and 0.25 M AlCl₃. The potential scan was initially conducted in the cathodic direction from 0 V vs. Mg in the potential range from -1.0 to 4.0 V at 10 mV s⁻¹.

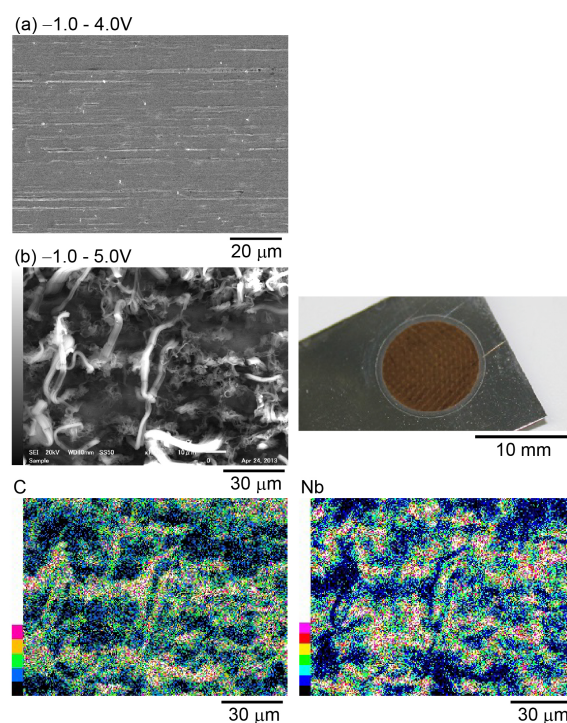


Figure 2. (a) SEM image of the Nb surface after cyclic voltammetry for 10 cycles in THF solution containing 0.50 M EtMgCl and 0.25 M AlCl₃ in the potential range from -1.0 to 4.0 V vs. Mg. (b) SEM and optical images and EDX mapping images of the Nb surface after cyclic voltammetry for 10 cycles in the same electrolyte from -1.0 to 5.0 V vs. Mg.

References

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