

Electrode Additives and the Rechargeability of the Alkaline Manganese Dioxide Cathode

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The performance of rechargeable alkaline Zn/MnO₂ cells is limited by capacity fade of the γ -MnO₂ cathode under deep discharge conditions ($>0.5e^-/\text{Mn}$). One strategy to overcome this is the incorporation of electrode additives, such as those based on alkaline earth or transition metal compounds, into the cathode mixture [1]. The inclusion of these compounds results in an increase in the cumulative discharge capacity, and cycle life, of rechargeable Zn/MnO₂ cells. Currently, the mechanisms by which these additive materials improve electrode cyclability remain unclear.

Previously we have shown that the inclusion of titanium dioxide in the electrode blackmix improves performance via the association of Ti(IV) ions with the γ -MnO₂ particle surface [2]. This association was examined using the combination of step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS). It was shown that electron/proton pairs are more easily able to intercalate into the γ -MnO₂ structure when Ti(IV) ions were associated with the surface, evident in Figure 1. Studies using time-of-flight secondary ion mass spectrometry (ToF-SIMS) were able to confirm this surface association, and also showed that Ti(IV) becomes incorporated into the γ -MnO₂ structure, in place of soluble Mn(III), upon cycling.

More recent electrochemical investigations have shed light on the role of Ba(II) compounds on the cyclability of the γ -MnO₂ cathode [3, 4]. These studies revealed that the presence of Ba(II) suppressed the dissolution of Mn(III) during the latter stages of discharge. In this manner Ba(II) inclusion prevents undesirable birnessite (δ -MnO₂) formation and significantly enhances electrode cyclability during deep discharge cycling. These studies suggested that an association of Ba(II) species with the γ -MnO₂ surface may underlie these improvements.

In this work, the combination of SPECS and EIS will be employed to examine features such as the charge transfer resistance (Figure 1), double layer capacitance, and bulk diffusion characteristics (Figure 2) at each step during charge-discharge cycling. By relating the modeled EIS response to changes which occur in the electrode, including the presence or absence of electrode additives, insights into the underlying mechanism will be outlined. ToF-SIMS studies on separate electrodes examined at a number of stages during cycling will also be used to probe any surface association, along with the incorporation of electrode additives into the porous MnO₂ structure.

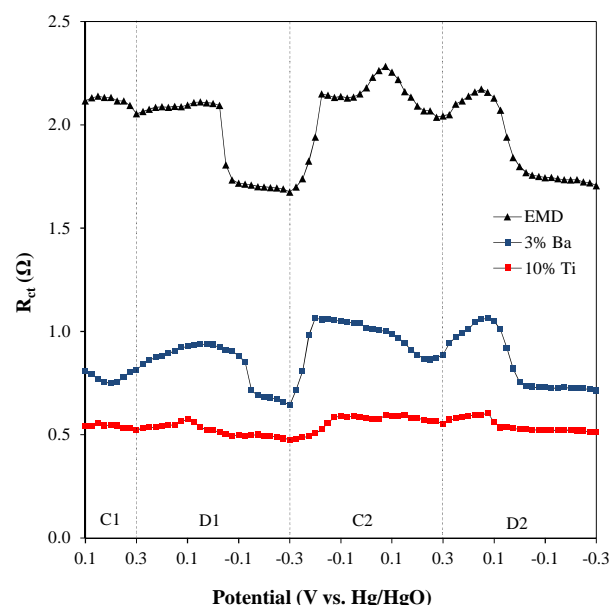


Figure 1. Variation in the charge transfer resistance for EMD, 3% Ba(OH)₂/97% EMD, and 10% TiO₂/90% EMD electrodes during charge-discharge cycling.

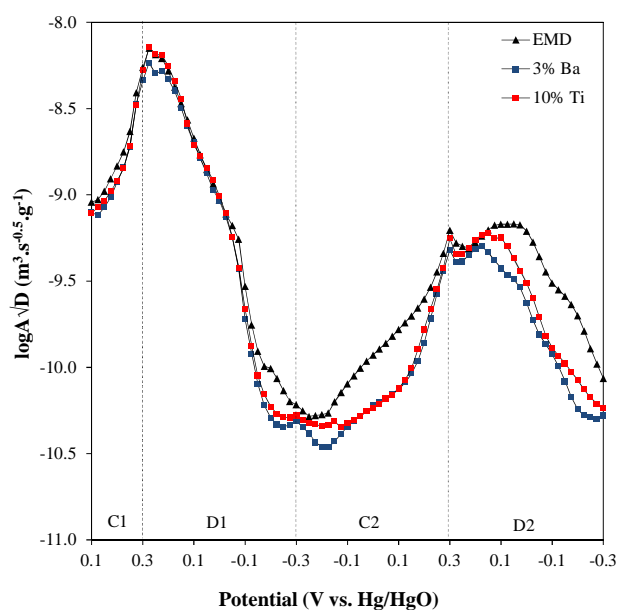


Figure 2. Changes in proton diffusion, expressed as $A\sqrt{D}$, during cycling of EMD in the presence of electrode additives.

REFERENCES

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