Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Self-discharge in Manganese Oxide Electrochemical Capacitor Electrodes in Aqueous Electrolytes with Comparisons to Faradaic and Charge Redistribution Models

Heather A. Andreas [*],[1], Jennifer M. Black, Alicia A. Oickle [2]

Department of Chemistry, Dalhousie University, Halifax, NS, B3H 4R2, Canada

ABSTRACT

The self-discharge profiles of manganese oxide films were examined to identify the self-discharge processes for these pseudocapacitive films. The profile shape was compared to four self-discharge models: an activation-controlled Faradaic reaction only; resistance-limited charge redistribution only; diffusion-limited charge redistribution only; or an activation-controlled Faradaic reaction coupled with charge redistribution. Hardware circuitry models (*e.g.* a transmission line) were used to model the activation-controlled reaction and resistance-limited charge redistribution. Ruthenium oxide was used as an experimental model for diffusion-limited charge redistribution, while highly porous carbon undergoing surface oxidation modelled the activation-controlled Faradaic reaction coupled with charge redistribution. Comparison of the manganese oxide self-discharge to these models showed an, as yet unidentified, activation-controlled Faradaic reaction on the manganese oxide surface, with a Tafel slope of 67 ± 5 mV. Additionally, the presence of charge redistribution was indicated in these films for the first time. During self-discharge, the activation-controlled reaction discharges the manganese oxide surface, setting up a potential differential between the surface and the bulk - where the surface has a lower potential. The result of this potential differential is that during charge redistribution the bulk manganese oxide provides charge to the surface, effectively slowing self-discharge.

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1. Introduction

Electrochemical capacitors, or supercapacitors, store charge in the electrode/electrolyte boundary, and through very fast redox reactions. The charge stored on the electrochemical capacitor can be lost when the capacitor is not in use, called self-discharge. Since electrochemical capacitors experience a higher rate of self-discharge than batteries, and because a loss in voltage results in less available energy and power, identifying the causes and mechanisms of self-discharge is important for these systems. Our focus is to ascertain the mechanisms of charge loss and to identify means for determining the reactions that cause the loss of charge, thereby allowing further study to prevent these reactions.

Self-discharge can arise from a number of possible reactions, including a parasitic Faradaic reaction or through movement of charge in the electrode. Possible Faradaic reactions that may occur in electrochemical capacitors using aqueous electrolytes include: the reaction of an electrolyte impurity, such as metal ion;[1–3] electrolyte decomposition or reaction of an oxygen impurity (small quantities of O_2 dissolved in the electrolyte or trapped in the material, e.g. in the pores), which is a particular problem in aqueous electrolytes where the stable voltage window is small and the electrolyte is often exposed to open atmosphere during cell preparation;[4,5] and, carbon oxidation of electrodes upon application of a positive potential (paper in preparation). The perceived loss of potential due to charge movement through the electrode material, so-called "charge redistribution", occurs because of incomplete charging throughout the bulk of the material resulting in a potential differential between the electrode surface and bulk. Charge redistribution has been identified in: metal oxides, such as ruthenium oxide,[6,7] which exhibit a diffusion-controlled charge movement; and, high surface area carbon electrodes, where the charge movement is limited by solution resistance in the pores.[8,9] Further complications in self-discharge analysis can arise due to

* Corresponding author. Tel.: +902 494 4505; fax: +902 494 1310.
  E-mail address: heather.andreas@dal.ca (H.A. Andreas).
[1] ISE Member
[2] Verschuren Centre for Sustainability in Energy and the Environment, Cape Breton University, Sydney, NS, Canada, B1P 6L2.

phase changes, such as those seen in manganese oxide, which can greatly influence the self-discharge profile shape,[10] though it is not believed that the phase changes are responsible for the self-discharge itself.

In 1997, Conway described three models which can be used to separate out the cause of self-discharge: an activation-controlled Faradaic reaction, a diffusion-controlled Faradaic reaction or ohmic leakage.[7,11] For the Faradaic reactions, identification of the reaction's rate-determining step focuses the search for the cause of the self-discharge, *e.g.* a profile exhibiting activation-controlled kinetics suggests that the dominating reaction does not involve a low concentration contaminant where diffusion may be expected to occur. The three rate-determining steps are expected to produce differently-shaped self-discharge profiles which can be separated through different plotting procedures. A self-discharge profile which exhibits a plateau followed by a linear potential drop when plotted as potential vs. the logarithm of self-discharge time is attributed to an activation-controlled mechanism.[7,11] A linear drop in potential exhibited when the data is plotted vs. $t^{1/2}$ is attributed to diffusion-controlled kinetics. [7,11] And, ohmic leakage between the positive and negative electrodes will result in a linearly dropping profile when the natural logarithm of potential is plotted vs. self-discharge time.[7,11]

Self-discharge due to charge redistribution has been studied by a number of groups,[8,9,12–17] particularly with respect to high surface area porous electrodes. The distributed resistance down a pore results in the potential at the tip of the pores changing more rapidly than the potential deeper in the pores, as shown by de Levie.[18,19] After charging of a highly porous electrode the distribution of potentials (or charge) caused by this pore effect will equilibrate, called charge redistribution. Since the electrode potential is measured at the tip of the pore, charge redistribution influences the potential measured and therefore changes the self-discharge profile. We have previously shown that charge redistribution down the pores in an electrode results in the same self-discharge profile as that resulting from an activation-controlled process (*i.e.* a plateau followed by a linear drop in potential when the self-discharge profile is plotted as a function of the natural logarithm of time).[8]

This paper provides several possible models for self-discharge caused by: 1) a sole activation-controlled Faradaic reaction; 2) resistance-limited charge redistribution; 3) diffusion-limited charge redistribution; and, 4) a coupled activation-controlled Faradaic reaction and charge redistribution. Hardware circuitry (such as a transmission line circuit) is used to model 1, 2 and 4. Model 3 is examined using self-discharge in hydrous ruthenium oxide electrodes. Model 4 is also examined experimentally using a highly porous carbon electrode which undergoes carbon oxidation during self-discharge. The self-discharge characteristics for these different models are provided, as well as a discussion of the relationship between these characteristics and the physical and chemical processes involved in self-discharge. By comparison with these models the self-discharge processes of experimental results can be interpreted.

The main focus of this paper is then an examination of self-discharge in manganese oxide films in aqueous electrolyte. While manganese oxide is gaining popularity as a pseudocapacitive material, to the best of our knowledge there are no in-depth studies of the self-discharge properties of these materials, other than the work of Hsu who showed that different phases of the manganese oxide result in differing final self-discharge potentials.[10] Typically, self-discharge rates are compared between electrode materials, without a discussion of the processes occurring on the electrode during self-discharge. In order to elucidate these self-discharge processes, in this paper the profiles of manganese oxide films are compared to the profile shape and characteristics of the models presented. Since
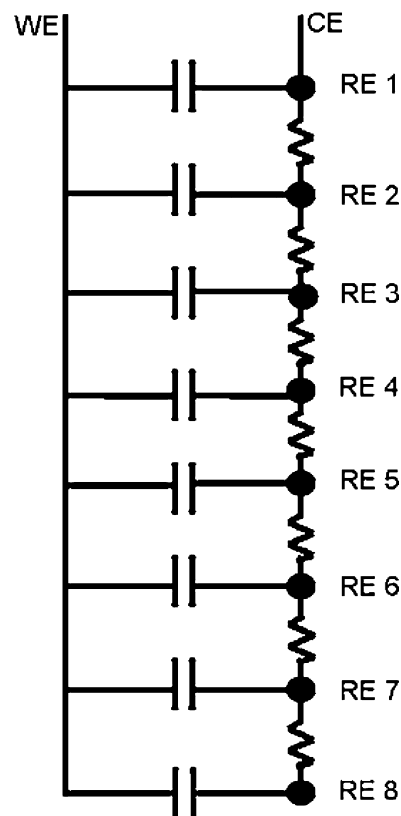

Fig. 1. Schematic of a transmission line hardware circuit, based on de Levie's model.[18,19].

the self-discharge kinetics of each electrode in a supercapacitor may be different, and to avoid convolution of the kinetics of the two electrodes, the self-discharge examined here focuses only the positive electrode (using a three-electrode, or half-cell configuration). Once the self-discharge of each electrode is well-established then further studies can incorporate both electrodes in full-cell supercapacitor self-discharge studies. This is the first in-depth analysis of manganese oxide self-discharge, including the first evidence for effects of charge redistribution through these films.

2. Experimental

2.1. Experimental Details for the Electronic Modeling of Charge Redistribution and Activation-controlled Reactions

Charge redistribution was modeled using a hardware transmission line circuit (Fig. 1). The circuit has been described in detail elsewhere.[8,9,14] Briefly, the circuit consisted of eight parallel sections containing a 100 μF capacitor and a 10 kΩ resistor in series. Each 100 μF capacitor was composed of a parallel combination of ten 10 μF/6.3 V multilayer ceramic chip capacitors. The capacitors were fully discharged (to 0 V) prior to each experiment.

Modeling of a Faradaic self-discharge reaction was done by drawing a current whose value was defined by the potential of the circuit, based on the Butler-Volmer equation. Again, this has been described elsewhere.[14] A 100-step galvanostatic cycling with potential limitation (GCPL) technique was composed using EC-Lab software (v.9.55–Bio-Logic). The reaction's Butler-Volmer parameters were modeled using: a one-electron transfer; a 0.75 V equilibrium potential; a 2×10^{-8} A cm^{-2} exchange current density; 0.5 for the symmetry parameter; and, a temperature of 298 K. This model was effective between 0.8 and 1.0 V on the circuit: below