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Modeling pseudo capacitance of manganese dioxide

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ABSTRACT

In order to better analyze and to explain the electrochemical and physical behavior during both charge and discharge of a manganese dioxide based ECs, an original electrochemical model is developed in this paper. The 1D model is an adaptation of the transmission line model (TLM), taking into account the cation diffusion in the solid oxide. A linear relation between redox potential and oxidation state is used and leads to a physical relation between its slope and the pseudo capacitance of the material, confirmed by an experimental investigation of cyclic voltammograms. The model can be applied for any metal oxide pseudo-capacitive material.

1. Introduction

Electrochemical supercapacitors (ECs, also called supercapacitors or ultracapacitors) are currently the subject of intense research due to the increasing use of energy storage devices in a large number of electrical/electronic systems. In ECs, two charge storage mechanisms can be involved [1,2]: the double layer storage and the pseudo-capacitance storage. In the first case the electrical capacitance is assured by the charge separation between a solid porous electrode and a liquid electrolyte. In the second case the pseudo-capacitance stems from ion chemisorption or from faradic redox reaction occurring at the interface between a material e.g. a transition metal oxide and a liquid electrolyte.

A great number of publications have presented mathematical models to help proper understanding of charge-discharge physical phenomenon in double layer electrodes. Most of these publications are based on the well-known Transmission Line Model (TLM), with electrical equation as a basis: charge transport and transfer balance [3–8]. Nevertheless, pseudo-capacitance electrodes category only has few publications concerning the storage process model. The most frequently modeled one is the faradic redox reaction of RuO_2 [9–11], for which computer simulations have been achieved starting from mathematical models but without comparing numerical results with experimental data.

Among the oxides showing a significant pseudo-capacitance, manganese dioxide has two advantages which make this material a promising one in this field [12]: low production cost and high compatibility with environmentally friendly aqueous electrolytes [13–16]. In spite of this, very few studies are devoted to the charge storage in this material [17–20]. Indeed, pseudo-capacitive behavior of MnO_2 based electrode originates from surface redox reactions and possible cation intercalation reactions in the tunneled structure of the manganese dioxide or in the lamellar structure, as the birnessite-type manganese dioxide [21]. Such coupled phenomena complicate the design of a proper model for this material.

In order to better analyze and to explain the electrochemical and physical behavior during both charge and discharge of a manganese dioxide based ECs, an original electrochemical model is developed in this paper.

The present study proposes a physical interpretation of the charge storage mechanism in MnO_2 through the use of a mathematical model and the determination of the physical parameters that control this storage, thanks to a comparison between the model and voltammetry measurements.

2. Model

2.1. Reaction kinetics and charge storage

A redox reaction, governed by a kinetic mechanism that can be modeled by the Butler–Volmer law, can be written as follows (Eq. (1)), where U is the interfacial potential and E_{eq} the equilibrium potential of the redox couple involved in the reaction

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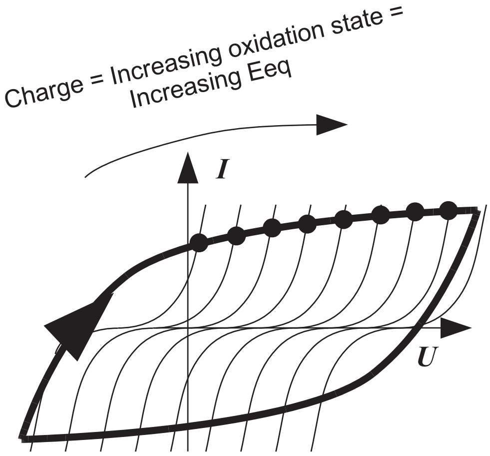

Fig. 1. Pseudo-capacitive material voltammogram.

(Eq. (2)). Only one electron is supposed to be involved in such a reaction, where j_0 is the value of the exchange current at the interface. Numerical simulations [10] show that, assuming a mass diffusion coefficient between 10^{-6} m^2 s^{-1} and 10^{-8} m^2 s^{-1}, no local depletion of electrolyte occurs in the porous medium. For a lower diffusion coefficient value, a local depletion can be envisioned, but its influence on the cell performance is rather weak. The ionic concentration in electrolyte is supposed to be uniform in space and constant in time in the model.

$$j_f = j_0 \cdot \left\{ \exp\left(\frac{\alpha \cdot (U - E_{eq}) \cdot F}{R \cdot T}\right) - \exp\left(-\frac{(1-\alpha) \cdot (U - E_{eq}) \cdot F}{R \cdot T}\right) \right\} \quad (1)$$

In the case of pseudo-capacitive materials, such as RuO_2 or MnO_2, the charge storage mechanism occurs in potential windows specific to each of these materials. From an electrochemical point of view, the particular behavior can be attributed to successive redox reactions occurring at different equilibrium potentials [2,11]. Another model has also been proposed [10]. It introduces a continuum of equilibrium potentials linked to the material average oxidation state. As the compound is oxidized, i.e. when its average oxidation state increases, the equilibrium potential of the Butler–Volmer law also increases according to a linear curve. As a consequence, the current vs. potential curve is continuously and reversibly shifted to higher (lower) potentials when the oxidation state increases (decreases). As shown in Fig. 1, a typical hysteresis is therefore induced when cyclic voltammetry experiments are performed.

In the case of MnO_2, surface redox reaction or intercalation can occur involving a cation A^+ (A^+ = alkaline earth cation or H+), leading to the decrease (or increase) of the manganese oxidation state from +IV to +III (respectively from +III to +IV):

$$\underbrace{MnO_2}_{4} + A^+ + e^- \underset{\text{Oxidation (charge storage)}}{\overset{\text{Reduction}}{\rightleftarrows}} \underbrace{MnO_2A}_{3} \quad (2)$$

Since MnO_2 is partially reduced at its natural state, the oxidation state variation occurring during a redox reaction can be calculated if it is possible to evaluate the amount of inserted cations (and therefore electrons) during the latter reaction:

$$\underbrace{MnO_2A_x}_{Os=4-x} + yA^+ + ye^- \rightleftarrows \underbrace{MnO_2A_{x+y}}_{Os=4-x-y} \quad (3)$$

At the microscopic level used in our model, this amount of inserted cations (n_{A^+}) can be calculated from Ficks diffusion equation that will be discussed in more details later on. The cation concentration is calculated at each position in the thickness of the electrode: the oxidation state is considered as a local value and no average calculation is used here. Because of the non-uniformity of the potential along the x axis in the electrode, the current crossing the interface between solid and liquid phase is not uniform. This leads to a non uniform flux of cation and, consequently, to a non uniform oxidation state in transient regime of cyclic voltammetry except at low scan rates. At low scan rates the value of the local cation concentration and of the local oxidation state become uniform, i.e. independent of the abscissa.

In our model, we assume a linear dependence between the equilibrium potential and the oxidation state:

$$E_{eq} = a \cdot Os + b \quad (4)$$

where Os is the local (i.e. at the solid-electrolyte interface) MnO_2 oxidation state. Such a variation is linked to the fact that, in Nernst equation, E_{eq} is directly linked to the oxidizing and reducing species. For solids this concentration is usually set to 1 but this is an approximation and activity coefficients are almost always unknown. If it is considered that the activity coefficient is dependent of state of charge a variation of the equilibrium potential versus oxidation state is observed as we postulate in Eq. (4). Such a behavior has been reported in the literature for RuO_2 [22] and MnO_2 [23] and was used in a similar model than in the present study [10]. This dependence of MnO_2 equilibrium potential as a function of charge state has been evidenced by X-ray absorption spectroscopy experiments [24,25,26–28].

2.2. Elementary analytical model

Supposing that during a cyclic voltammetry experiment, the material behavior is similar to a pure electrical capacity, the relation between the intensity and the voltage variation is described by the fundamental relation:

$$q = C \cdot U \text{ or } I = C \cdot \frac{dU}{dt} = \pm C \cdot V_{sc} \quad (5)$$

where (dU/dt) is the scan rate V_{sc} (of a constant absolute value) of the cyclic voltammetry experiment, q is the stored charge and C is the capacitance. The current intensity (I) has therefore a constant value during both charge and discharge processes: +I during the increasing potential segment, and −I during the decreasing potential segment.

As previously stated, the manganese oxidation state is +IV when no cation is inserted in the solid, thus corresponding to the maximum theoretical electrode state of charge. When a certain amount n_{A+} of cations is intercalated into the solid, the oxidation state is given by the following relation:

$$Os = Os_{\max} - \frac{n_{A^+}}{n_{MnO_2}} = Os_{\max} - \frac{I \cdot t}{F \cdot n_0} \quad (6)$$

In this equation, n_0 is the total amount of Mn mole (per volume unit) in the solid available for the redox reaction and ($I{\cdot}t/F$) is the amount of cations moving during the discharge process between the [0 t] time slot. According to [4] the equilibrium voltage as a function of time, can be expressed as:

$$E_{eq} = Os \cdot a + b = Os_{\max} \cdot a - \frac{a \cdot I \cdot t}{F \cdot n_0} + b \quad (7)$$

Considering that the exchange current value of the redox reaction (3) must be sufficiently high, only a small electrode overpotential would be measured by electrochemistry experiments. In the opposite case (case of a low exchange current value material), the temporal response is considered as too slow (see Section 4.2)