Electrochemical impedance spectra of $V_2O_5$ xerogel films with intercalation of lithium ion

ZHANG Yong (张勇)1,2, LIU Yu-wen (刘玉文)2, CHENG Yu-shan (程玉山)2, HU Xin-guo (胡信国)1
(1. Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China; 2. Jiangmen JJJ Battery Company Limited, Jiangmen 529000, China)

Abstract: Vanadium pentoxide xerogel films used for lithium rechargeable batteries were prepared from crystalline $c-V_2O_5$ by melt quenching method, then the electrochemical process of lithium intercalation into vanadium pentoxide xerogel films was simulated with an equivalent circuit model, which was derived from the mechanism of electrode reactions. Measured electrochemical impedance spectra at various electrode potentials were analyzed by using the complex non-linear least-squares fitting method. The results show that impedance spectra consist of 2 high-to-medium frequency depressed arcs and a low frequency straight line. The high frequency arc is attributed to the absorption reaction of lithium ions into the oxide film, the medium frequency arc is attributed to the charge transfer reaction at the vanadium oxide/electrolyte interface and the low frequency is characterized by a straight line with a phase angle of 45° corresponding to the diffusion of lithium ion through vanadium oxide phase. The experimental and calculated results are compared and discussed focusing on the electrochemical performance and the state of charge of the electrode. Moreover, the high consistence of the fitted values of the model to the experimental data indicates that this mathematical model does give a satisfying description of the intercalation process of vanadium pentoxide xerogel films.

Key words: vanadium pentoxide xerogel films; electrochemical impedance spectra; equivalent circuit; melt quenching method; lithium rechargeable batteries

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1 INTRODUCTION

Vanadium pentoxide xerogel (VXG) films have received significant attention during the last two decades due to their broad industrial applications especially in optical switching devices1,2, electrochromic devices3 and reversible cathodes for lithium rechargeable batteries. The common methods of preparing VXG films are conventional techniques, including pulsed laser deposition4, sputtering5 and vacuum-deposition6. However, such methods always involve conditions of high temperature and vacuum, which require complicated techniques and costly facilities.

Since electrochemical intercalate and deintercalation are in general limited by the rate of diffusion of the ion in the oxide electrode, the attention of previous works has been focused on the determination of diffusivity in the electrode materials. In contrast, the mechanism by which lithium ions intercalate the VXG films electrode has received little attention7. Moreover, a variety of reported interpretations of the impedance spectra measured with intercalation electrodes such as VXG films have been discussed and used in the literature, but there is still a need for further investigations to clarify the reaction mechanism and the rate limiting processes of VXG. In this article, VXG films electrode was electrochemically investigated by means of electrochemical impedance spectra (EIS), to increase the understanding of the impedance response measured with the film electrode and to critically examine the general accepted description of the intercalation process of this material. For the analysis, a theoretical mathematical EIS model was derived, and fitting the model to the experimental data obtained with the different electrode potentials validates its reaction mechanism. The variations of the resulting kinetic parameters with the state of discharge were evaluated and discussed.

2 EXPERIMENTAL

2.1 Fabrication of VXG film electrodes

VXG film electrodes were prepared by melt quenching method. The process is shown schematically in Fig. 1. The powder of $c-V_2O_5$ was first put into alumina crucible, then was calcined in a muffle furnace at 800 °C for 20 min and the melt liquid was
fast poured into de-ionized water at ambient temperature and stirred vigorously.

The wet gels were aged for 48 h at room temperature in sealed test tubes. The longer aging time in open tubes, the better gels had mechanical integrity. After aging, the sample was used to deposit thin films on nickel mesh substrate by spin coating at 1 200 r/min using a Headway spincoater. Before being introduced into the glove box, the electrodes were heated in vacuum oven at 150 °C for 48 h.

2.2 Electrochemical measurements

Unless stated otherwise, a three-electrode polyethylene cell with a parallel plate configuration was employed for the electrochemical measurements. A nickel mesh current collector covered with a VXG film served as a working electrode, whereas 2 lithium foils were used as reference and counter electrodes. The electrochemical measurements were carried out in 1 mol/L LiPF₆ + propylene carbonate (PC) solutions. EIS were measured on the film electrode by using ZAHNER IM6e. The impedance spectroscopy was conducted from 50 mHz to 100 kHz at amplitude of 5 mV. EIS test began by discharging with a constant current at a rate of 60 mA/g to the specified open circuit voltage. Before performing EIS measurements, the potential was set and held at the desired value for at least 1 h. The current was stable and lower than 100 pA, which denoted that Li concentration has reached the equilibrium in the whole particle. All the electrochemical experiments were performed at 25 °C in a glove box filled with purified Ar gas.

3 RESULTS AND DISCUSSION

3.1 Mathematical model and equivalent circuit model

Previous reports showed that the impedance spectrum analysis of a vanadium oxide film electrode in contact with a liquid electrolyte that penetrates the pores can be modeled by a modified Randles equivalent circuit[5] by using a resistor/capacitor (R/C) combination. In fact the presence of an additional dipole may account for at least 2 physical processes[5]; the adsorption process of Li⁺ or other species onto the surface of the electrode without charge transfer; the formation of a surface layer on the electrode. In the latter case, the surface electrode would be covered by an ionically conducting but electronically insulating surface layer. However, since the 2 capacitive loops cannot be distinguished from the impedance spectra in the present results, so the equivalent circuit in Fig. 2(a) was selected to examine the experimental results. Cₓ is the double-layer capacitance due to the accumulation of charged species in the electrolyte at the interface, Cₓ is the capacitance arising from the adsorption of lithium ion into the oxide film, Rₓ is the resistance of electrolyte, Rₓ is the resistance associated with the absorption reaction of adsorbed lithium ion into the oxide film, Rₓ is the resistance associated with charge transfer at the electrolyte-cathode VXG films interface and Zw is the Warburg impedance for the diffusion of lithium ion through the oxide film. In order to consider semicircles with a depressed shape, the commonly used capacitor Cₓ is replaced with constant phase elements Qₓ given by \( Z(Q) = \frac{1}{Y_i(j\omega)^{-n}} \), where \( \omega \) is the angular frequency, \( Y_i, j \) and \( n \) are the constant, and \( 0 \leq n \leq 1 \). When \( n \) is 1, \( Q \) becomes an ideal capacitor.

![](image1)

**Fig. 2** Model of VXG films electrodes
(a)—Equivalent circuit; (b)—Simplified equivalent circuit; (c)—Nyquist plot of complex impedance circuit

3.2 Model deduction and analysis of impedance data

It is generally agreed that the Warburg imped-