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Electrochimica Acta 52 (2007) 2009–2017
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Theoretical approach to cell-impedance-controlled lithium transport through $Li_{1-\delta}Mn_2O_4$ film electrode with partially inactive fractal surface by analyses of potentiostatic current transient and linear sweep voltammogram

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Received 17 May 2006; received in revised form 14 July 2006; accepted 5 August 2006
Available online 14 September 2006

Abstract

Lithium transport through the partially inactive fractal $Li_{1-\delta}Mn_2O_4$ film electrode under the cell-impedance-controlled constraint was theoretically investigated by using the kinetic Monte Carlo method based upon random walk approach. Under the cell-impedance-controlled constraint, all the potentiostatic current transients calculated from the totally active and partially inactive fractal electrodes hardly exhibited the generalised Cottrell behaviour and they were significantly affected in shape by the interfacial charge-transfer kinetics. In the case of the linear sweep voltammogram determined from the totally active and partially inactive fractal electrodes, all the power dependence of the peak current on the scan rate above the characteristic scan rate deviated from the generalised Randles–Sevčik behaviour. From the analyses of the current transients and the linear sweep voltammograms simulated with various values of the simulation parameters, it was further recognised that the cell-impedance-controlled lithium transport through the partially inactive fractal $Li_{1-\delta}Mn_2O_4$ film electrode strongly deviates from the generalised diffusion-controlled transport behaviour of the electrode with the totally active surface, which is attributed to the impeded interfacial charge-transfer kinetics governed by the surface inhomogeneities including the fractal dimension of the surface and the surface coverage by active sites and by the kinetic parameters including the internal cell resistance.

Keywords: Fractal $Li_{1-\delta}Mn_2O_4$ film electrode; Cell-impedance-controlled constraint; Partially inactive surface; Potentiostatic current transient; Linear sweep voltammogram

1. Introduction

In order to solve problems arising from the irregular interface in various electrochemical processes, such as rough, porous and partially inactive interface have effectively been modelled as fractal [1–3]. Especially, mass transport towards the irregular interface in the electrochemical system has extensively been studied by potentiostatic current transient technique [4–9], linear sweep voltammetry [8,10–14] and ac-impedance spectroscopy [15–18]. When mass transport is purely controlled by the diffusion process, the electrochemical responses at the irregular interface obey the generalised forms [8] of the Cottrell, Randles–Sevčik and Warburg relation.

However, it has been reported that lithium transport through transition metal oxides and carbonaceous materials [9,19–22] is limited by the internal cell resistance R_{int} at the electrolyte/electrode interface, and it is then coupled with the lithium diffusion in the electrode. In parallel, it has also been concluded that hydrogen transport through hydride-forming metals and alloys [23–25] proceeds under the condition where hydrogen diffusion in the electrode is kinetically mixed with the charge-transfer reaction at the electrolyte/electrode interface.

In this respect, we recently theoretically as well as experimentally investigated the transport phenomena of lithium through the $Li_{1-\delta}CoO_2$ film electrode with rough surface under the cell-impedance-controlled constraint [26,27]. From the analyses of the potentiostatic current transients and the linear sweep voltammograms theoretically and experimentally determined, it was strongly suggested that the beneficial contribution of the surface roughness to the cell-impedance-controlled lithium

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doi:10.1016/j.electacta.2006.08.010

transport counterbalances that detrimental contribution of the internal cell resistance.

In reality, the electrode surfaces are not totally active in atomic and geometric scales, and thus atomic transport through the electrode with the partially inactive surface may be inevitably affected by the surface inhomogeneities [4]. However, relatively little attention has been paid to atomic transport through the partially inactive fractal electrode under the dominant influence of the interfacial charge-transfer reaction, in spite of its importance.

The present work is concerned with the transport phenomena of lithium in the $Li_{1-\delta}Mn_2O_4$ film electrode with the partially inactive fractal surface under the cell-impedance-controlled constraint. By using the kinetic Monte Carlo method based upon random walk approach [28–30], the potentiostatic current transient and the linear sweep voltammogram were calculated from the well-defined fractal profiles with various dimensions. Then, we finally determined the characteristic time t_{ch}, i.e. time to transition of semi-infinite diffusion to finite diffusion, and the characteristic scan rate ν_{ch}, i.e. scan rate to transition of finite diffusion to semi-infinite diffusion, to explore the effects of the surface inhomogeneities and the internal cell resistance on the cell-impedance-controlled lithium transport through the partially inactive fractal electrode based upon the simulated data.

This work is the preceding theoretical step of the collective programme of elucidating the roles of such surface inhomogeneities as the fractal dimension of the surface and the surface coverage by active sites and of such kinetic parameters as the internal cell resistance in the cell-impedance-controlled lithium transport through the $Li_{1-\delta}Mn_2O_4$ film electrode. It is certain that the theoretically results obtained in this work will be a milestone to analyse the experimental data of the potentiostatic current transient and the linear sweep voltammograms measured from the $Li_{1-\delta}Mn_2O_4$ film electrode with the partially inactive fractal surface in continuing future experimental work.

2. Fractal profiles and random walk simulation

Now, let us introduce the Cantor set, which has been used to model the partially inactive surface, in order to obtain a single-valued fractal profile [2–4,15]. Fig. 1 shows the schematic diagram of producing the Cantor set fractal profile. Firstly, a line with unit length is divided into three equal parts and then the central part is removed leaving its end parts. This process is then applied again to each of the two remaining parts and so on. In this work, the segments of the Cantor set are assumed to be active sites for lithium transport, and regions between them to be inactive sites. As expected, the surface coverage by active sites θ decreases with each iteration. Here, θ represents the fraction of the area of active sites to total surface area. The fractal dimension d_F of this Cantor set is known to have the value of $\ln 2/\ln 3 \approx 0.631$ [2–4]. In the simulation of the current transient and the linear sweep voltammogram, three different fractal profiles with $d_F = 1.00$ (totally active surface), 0.732 ($\approx \ln 5/\ln 9$) and 0.631 ($\approx \ln 2/\ln 3$) were employed as the interface boundary between the electrolyte and the electrode.

In this study, the potentiostatic current transient and the linear sweep voltammogram were computed largely based upon the kinetic Monte Carlo algorithm which had been well established in the former research works about lithium transport through the flat electrodes of transition metal oxides [29,30], except that the fractal profiles with the partially inactive surface were used as the electrolyte/electrode interface.

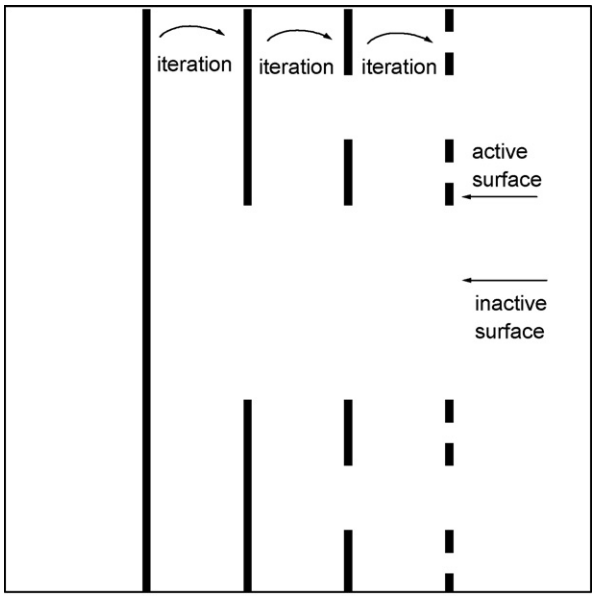

Fig. 1. Schematic diagram of producing the Cantor set fractal profile by iterative removal of the central part of a line segment.

The simulation procedure is briefly described as follows: firstly, the electrode lattice sites are randomly filled with atoms to a predetermined fraction by the initial electrode potential E_{ini}. Secondly, each atom is allowed to perform a random walk to one of four neighbouring lattice sites under the constraint that two atoms cannot simultaneously occupy the same lattice site. Here, one trial change in the configuration of the lattice corresponds to one Monte Carlo step (MCS). Thirdly, when an atom reaches the electrolyte/electrode interface, the jump probability of atom W_{tr} across the electrolyte/electrode interface is calculated from the boundary condition at the interface.

According to the cell-impedance-controlled constraint, the jump probability of atom W_{tr} across the electrolyte/electrode interface is given by [29,30],

$$W_{tr} = f|E_{eq} - E_{app}| \propto \frac{\Delta E}{R_{int}} \quad (1)$$

where f designates the dimensionless conversion factor which simply inversely proportional to the internal cell resistance R_{int}, and $|E_{eq} - E_{app}|$ represents the potential difference ΔE between the electrode potential E_{eq} and the applied potential E_{app} in absolute value. Here, W_{tr} is mainly determined by $|E_{eq} - E_{app}|$ as well as f. E_{app} is strongly dependent upon time and scan rate, and E_{eq} is a function of the concentration of atoms at the electrolyte/electrode interface. In this work, f was arbitrarily taken as the value below unity, keeping in mind that the current under the cell-impedance-controlled constraint is always lower in value than that current under the diffusion-controlled constraint. Accordingly, W_{tr} in Eq. (1) is the dimensionless parameter with the value below unity ($0 \leq W_{tr} < 1$). In the case of