



Electrochemical Impedance Spectroscopy Illuminating Performance Evolution of Porous Core–Shell Structured Nickel/Nickel Oxide Anode Materials



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ABSTRACT

The electrochemical reaction kinetics of the porous core–shell structured Ni/NiO anode for Li ion battery application is systematically investigated by monitoring the electrochemical impedance evolution for the first time. The electrochemical impedance under prescribed condition is measured by using impedance spectroscopy in equilibrium conditions at various depths of discharge (DOD) during charge–discharge cycles. The Nyquist plots of the binder-free porous Ni/NiO electrode are interpreted with a selective equivalent circuit composed of solution resistance, solid electrolyte interphase (SEI) film, charge transfer and solid state diffusion. The impedance analysis shows that the change of charge transfer resistance is the main contribution to the total resistance change during discharge, and the surface configuration of the obtained electrode may experience significant change during the first two cycles. Meanwhile, the increase of internal resistance reduced the utilization efficiency of the active material may be another convincing factor to increase the irreversible capacity. In addition, the impedance evolution of the as-prepared electrode during charge–discharge cycles reveals that the slow growth of the SEI film is responsible for the capacity fading after long term cycling. As a result, several strategies are summarized to optimize the electrochemical performances of transition metal oxide anodes for lithium ion batteries.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) with superior working potentials and high energy density are highly desired due to its extended application in the coming era of electric vehicles (EVs) and/or hybrid electric vehicles (HEVs) [1–4]. However, the energy density and safety performance of current dominant LIBs with graphite anode are still below the requirements of EV development [5]. Among several compounds proposed to replace graphite at the negative electrode, 3d transition metal oxides (TMOs, where M is Fe, Co, Ni, and Cu) have been widely investigated as promising anodes for LIBs since Tarascon et al. for the first time reported the electrochemical performance of CoO toward lithium [6]. For

example, the three-dimensional NiO film exhibited a promising capacity of 560 mA h g^{-1} with capacity retention of 97% after 100 cycles [7]. As we previously reported, the NiO–Ni composite anode showed high capacity retention of 95.1% over 100 cycles [8].

As well known, the electrochemical reaction mechanism of TMOs with Li differs from the classical Li intercalation/deintercalation or Li-alloying process, but involves the formation and decomposition of Li_2O [1,9], which ensures higher theoretic capacities ($600\text{--}1000 \text{ mA h g}^{-1}$) and higher charge–discharge potentials (i.e. high safety). However, the Coulombic efficiencies and cycling performances of TMO anodes are not satisfied. It is commonly attributed to the formation of SEI film, poor conductivity, large volume change of active materials, and/or incomplete decomposition of Li_2O during the charge–discharge processes. Accordingly, various novel surface modifications and original nanostructure fabrications have been developed to improve the electrical conductivity, buffer the volume expansion, and enhance the electrochemical activity of TMOs [10–13]. However, it is still absence of theory support to effectively overcome the

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shortcomings of TMOs. Therefore, it is necessary to make more efforts to understand the impacts of their electrochemical reaction kinetics on electrochemical performance during charge–discharge cycles to further enhance battery performance.

Electrochemical impedance spectroscopy (EIS) is a powerful electrochemical analytical technique to study the electrochemical behaviors involved in the electrodes of LIBs. This important technique could provide the kinetics information of the electrochemical reaction in the electrode. Therefore, the evolution of the electrochemical and physical properties of the electrodes can be inferred from EIS. In recent years, EIS has been rigorously applied in explaining the topotactic insertion reaction [14–17], as well as the Li-alloying reaction process [18–21]. However, for the conversion-reaction type materials, little work was reported to focus on the electrochemical impedance features of TMOs due to their complex reactions with lithium [22]. More importantly, to the best of our knowledge, in previous studies, the working electrodes involving TMOs inevitably contained the conductive additive and polymer binder. The existence of in-active materials possibly affects lithium ion migration, and causes the complicated electrochemical response signal, which shows some difficulties in clearly illustrate the TMO reaction kinetics with lithium. For example, Xiang et al. introduced the two-parallel diffusion path EIS model to investigate and analyze the corresponding impedance response signal of the CuO nanoplates electrode to obtain the kinetics parameters [22]. Therefore, a design of binder-free and conductive additive-free electrode is better for a more direct insight into the electrochemical processes kinetics of TMOs. Based on this purpose, in this study, we design core–shell structured Ni/NiO electrode without binder and conductive additive, and study its impedance responses at different depths of discharge (DOD) and variations as a function of cycle number. Furthermore, comparing the electrochemical performance with the EIS results, we attempt to acquire a better understanding of the capacity fading mechanism of the NiO electrode using EIS, and could also obtain the information to optimize the electrochemical performances of the NiO electrode and even other TMOs.

2. Experimental Details

2.1. Material preparation

The porous core–shell structured Ni/NiO electrode without binder and carbon black was synthesized via a conventional solid state reaction. In a typical synthesis, the pre-treated commercial porous Ni foams were punched in the form of 14 mm diameter disks. Then the Ni foams were placed into a muffle furnace and fired at 500 °C in air.

2.2. Structural Characterization

X-ray powder diffraction (XRD) was performed on a D-5000 X-ray diffractometer at the 2θ range of 20° to 90° using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). Traces software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files was used to identify the product phases. The morphologies of the obtained samples before and after heat treatment were observed by JEOL JSM-6330F type field emission scanning electron microscopy (FE-SEM) under 10 kV accelerating voltage.

2.3. LIB Electrode Fabrication and Performance Measurements

CR-2032-type coin cells were assembled in an Ar-filled dry glove box. The as-prepared NiO electrodes were used as working electrodes, lithium foil as the counter electrode and reference

electrode, and the porous polypropylene as the separator. The electrolyte was 1 M LiPF₆ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylene methyl carbonate (EMC) (1:1:1 by volume). The galvanostatic cycling with potential limitation were performed using a NEWARE BTS-610 battery tester at room temperature. The current density was fixed at 156 mA g⁻¹ in this study, and the specific capacities calculated were normalized by the weight of NiO that can be easily calculated based on the weight difference of Ni foam before and after oxidation. The EIS were systematically measured at different depths of discharge and during subsequent charge–discharge cycles using VersaSTAT 200 electrochemical workstation with the frequency ranging from 100 kHz to 5 mHz and an AC signal of 5 mV in amplitude as the perturbation. The cells under prescribed cutoff condition were relaxed for 6 h until they obtained a relative equilibrium condition. The EIS data were fitted with Zview computer program to analyze the individual resistances. In addition, it is particularly worth mentioning that the fitting error is usually less than 1% in the proposed model.

3. Results and Discussion

3.1. General characterization of the core–shell structured Ni/NiO electrode

Fig. 1 (a) presents the XRD patterns of the Ni foam before and after heating treatment. The vertical lines on the x-axis correspond to the standard XRD reflections of cubic Ni and rhombohedral NiO. As seen in Fig. 1(a), the Ni foam before heating showed three diffraction peaks centred at 44.53°, 51.88° and 76.42°, corresponding to Ni (111), (200) and (220) planes (Space group Fm-3m (225), JCPDS No. 04-850), respectively. The heating treatment of Ni foam causes three diffraction peaks observed at $2\theta = 37.3^\circ, 43.3^\circ$ and 62.9° that can be assigned to NiO (101), (012) and (110) faces (Space group R-3m (166), JCPDS No. 44-1159), respectively. No other diffraction peaks can be observed, indicating no redundant phase in the final product. The cell structures of both cubic Ni and rhombohedral NiO are shown in Fig. 1(b). It can be clearly observed that oxygen atoms were regularly embedded into the lattice of Ni through the specific oxidation process resulting in the formation of NiO.

The surface of pristine Ni foam was relatively smooth, and the grain boundaries of metallic Ni were apparent (see the inset of Fig. S1(b)). The core–shell structured Ni/NiO can be confirmed by Fig. 1(c) that shows the cross sectional image of the Ni foam after oxidation. It can be clearly seen that NiO was uniformly formed on both sides of Ni skeleton. The relatively smooth surface was changed into coarse features after heating treatment, and nano-sized NiO features were observed (Fig. 1(d)). More interestingly, irregular porous structures with the dimension of about 200 nm can also be found in the inset of Fig. 1(d). This porous core–shell structure was significantly different from the Ni foam before oxidation (see Supporting Information, Fig. S1). As shown in Fig. S1 (a), Ni foam displayed a three-dimensional structure. Moreover, the cross sectional image (Fig. S1(b)) of the pristine Ni foam showed no obvious stratification and/or tegmen. Apparently, the aforementioned features formed during calcinations of Ni foam results from oxidation reaction, which was beneficial to the electrolyte access into NiO. Therefore, the porous core–shell structured Ni/NiO anodes are expected to show good electrochemical performance.

The voltage profile, cycling performance and Coulombic efficiencies of the porous core–shell structured Ni/NiO electrode over 65 cycles are shown in Fig. 2. It can be observed that the 1st discharge capacity delivered was around 997 mA h g⁻¹, and the capacity was found to be decreased to 701 mA h g⁻¹ in the 2nd

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