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

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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 Li₂O [19], which ensures higher theoretic capacities (600–1000 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 Li₂O 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
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 Kα radiation (λ = 1.5405 Å). 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), (20 0) and (2 2 0) planes (Space group Fm¯-3m (2 2 5), JCPDS No. 04-850), respectively. The heating treatment of Ni foam causes three diffraction peaks observed at 2θ = 37.3°, 43.3° and 62.9° that can be assigned to NiO (1 0 1), (0 1 2) and (1 1 0) 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 calculations 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 mAh g⁻¹, and the capacity was found to be decreased to 701 mAh g⁻¹ in the 2nd
cycle. More importantly, the first and second discharge curves were significantly different, revealing a variation of the Li intercalation reaction process, which was very similar with the other TOMs reported in the literatures [8,11,22]. In addition, after 65 cycles, the discharge capacity remained about 646 mA h g\(^{-1}\), which indicated the high capacity retention of the obtained Ni/NiO electrode. Normally, the nanostructured anodes show the relatively low Coulombic efficiency in the first cycle due to side reaction between the anodes and the electrolyte [7,8,19,22]. The Coulombic efficiency of the porous core–shell structured Ni/NiO electrode (Fig. 2) can reach as high as 75.88\%, confirming high reversible advantage of porous core–shell structure. In the sequent cycles, the Coulombic efficiencies were over 98%.

### 3.2. Equivalent circuit and typical fitting parameters

Used a suitable equivalent circuit to simulate the electrochemical impedance has been considered as a powerful method to obtain the electrochemical reaction kinetics parameters. The previous studies reported various equivalent circuits from the classical Randles circuit to more complex systems built by several sub-circuits for simulating the different Nyquist plots [17–19,22–24]. In our case, however, the binder-free thin film electrode holds larger or smaller pores that can be effectively filled by the liquid electrolyte (Fig. 1(c) and (d)), which is remarkably consistent with thin transition metal oxide electrodes reported by Aurbach and co-workers [25]. Therefore, an extremely similar equivalent circuit exhibited in Fig. 3 was employed to study the measured impedances. As shown in Fig. 3, the equivalent circuit composes of an ohmic resistance (R\(_s\)), two RC parallel elements in series.
describing the SEI film on the surface ($R_{\text{SEI}}$ and $CPE_{\text{SEI}}$) and lithium ion charge transfer at interface ($R_{\text{ct}}$ and $CPE_{\text{ct}}$), and Warburg impedance for solid state diffusion of lithium ions. A constant phase element (CPE) was used in the equivalent circuit instead of a pure capacitance due to the inhomogeneous surface of the thin film working electrode. $CPE_{\text{SEI}}$ and $CPE_{\text{ct}}$ are constant phase elements corresponding to the surface film and double layer capacitance [26–28]. It is worth mentioning that the passivation SEI layer may not be formed on the working electrode surface at low DOD during the first cycle because the reduction potential (lowest unoccupied molecular orbital) of common organic liquid electrolyte is near 1.0 V versus Li$^+$/Li$^0$ [29]. In other words, the organic liquid electrolyte at high potential (low DOD) could not be reduced to create a SEI film [30,31]. Therefore, the operational equivalent circuit will exclude the $R_{\text{SEI}}$ and $CPE_{\text{SEI}}$ circuit elements (blue box in Fig. 3) in a few rare cases such as the low DOD during the first cycle.

A typical fitting plots of this core–shell structured Ni/NiO anode is illustrated in Fig. 4, where the data of the ac impedance responses was measured at 0.7 V vs. Li$^+$/Li in the 10th Li-intercalation (about 80% DOD). The dotted curve in Fig. 4 shows the impedance calculated using the equivalent circuit. The error between the experimental and calculated data was less than 1%. The fitting parameters obtained from the equivalent circuit are presented in Table 1. Note that two depressed semicircles (Fig. 4) related to the SEI film and charge transfer in the high-medium frequency region can be effectively simulated using the constant phase elements ($CPE_{\text{SEI}}$ and $CPE_{\text{ct}}$), which in turn proved the reliability of the selective equivalent circuit (Fig. 3).

### Table 1

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$R_s$ (Ω)</th>
<th>$CPE_{\text{SEI}}$</th>
<th>$CPE_{\text{ct}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEI</td>
<td>5.290</td>
<td>1.40E-06</td>
<td>1.001</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>29.54</td>
<td>5.68E-05</td>
<td>0.7964</td>
</tr>
<tr>
<td>Diffusion</td>
<td>182.5</td>
<td>1.333</td>
<td>0.4526</td>
</tr>
</tbody>
</table>

#### 3.3. Impedance depending on the depths of discharge

The electrode structure can be significantly influenced by the Li-ion charge/discharge depth, consequently leading to the variation of the state of the electrode/electrolyte interface. Fig. 5(a) and (b) show the Nyquist plots of the electrode at different discharge potentials in the first and second cycles, respectively. The shapes of Nyquist plots were very similar along with the increasing discharge depth. In other words, all Nyquist plots consisted of a depressed semicircle where a high-frequency semicircle (HFS) and a medium-frequency semicircle (MFS) overlap each other and a low long-frequency line (LFL) except the low discharge depth Nyquist plots in the first cycle. However, it can be observed in Fig. 5 that the individual resistances at each step upon different discharge potentials undergone obvious changes, indicating the significant changes of the reaction kinetics process. The dependences of fitted resistance parameters on discharge potential during the initial two cycles are shown in Fig. 6. Clearly, the variation of the values for $R_s$, $R_{\text{SEI}}$, and $R_{\text{ct}}$ during the first cycle was more apparent than those of the second cycle. To be specific, in the first discharge process, the values of $R_s$ increased firstly with the increasing discharge depth, and then dropped to a low point (Fig. 6a), which was significantly different from the previous studies due to this binder-free working electrode [22,32]. The rise
in $R_s$ can be attributed to two reasons: one was the electrode pulverization originating from the formation of Li$_2$O through conversion-reaction; the other was the growth of a thicker SEI film, which was in highly accordance with the variation tendency of $R_{sf}$ (Fig. 6b). However, the fall in $R_s$ with the increasing discharge depth can be mainly ascribed to the partial dissolution or decomposition of the as-produced SEI film owing to the highly catalytic activity of the electroproduced Ni metal particles at low discharge potential [33,34]. Moreover, the variation tendency was the opposite in the values of $R_{ct}$ with the increasing discharge depth (Fig. 6c). This is very similar to the behavior of the silicon electrodes reported by Ruffo and co-workers [19]. On the one hand, when NiO anode was discharged, NiO decomposed into many smaller one composing of Li$_2$O and metal Ni, which increased the surface area of the electrode. The sufficient contact between the active material and the electrolyte led to the enhanced electrode activity and reduced the impedance of $R_{ct}$. On the other hand, the larger electrode surface resulted in the formation of more new SEI on fresh pulverization electrode, which may destroy the porous structure of the working electrode, and thus block the diffusion path of the lithium ion into the electrode. Conversely, the variation of the values for $R_s$, $R_{sf}$, and $R_{ct}$ during the second cycle was relatively mild. Meanwhile, the main contribution to the total resistance of discharge state can be attributed to $R_{ct}$ change. Therefore, it can be concluded that the working electrode reached a relatively stable state after the first discharge–charge cycle. Interestingly, the values of $R_s$, $R_{sf}$ and $R_{ct}$ at the discharge potential of 2.1 V in the second cycle were relatively low compared with those values at the discharge potential of 0.02 V in the first cycle. This was expected because the electrode structure may be affected by the charge process, such as the partial decomposition of SEI layer [22]. In addition, as discussed in section 3.1, the low Coulombic efficiency resulted from large irreversible capacity loss in the first cycle is generally ascribed to the formation of SEI film. However, based on the aforementioned results, the increase of the internal resistance ($R_s$) resulted from the pulverization and degradation of the electrode that reduced the utilization efficiency of the active material could be another convincing reason to increase the irreversible capacity in the first cycle. Meanwhile, it is noted that the well-defined plateau observed in the first discharge (Fig. 2) vanished on subsequent discharges, leading to sloppy

Fig. 6. The fitted parameters of (a) ohmic resistance ($R_s$), (b) SEI film resistance ($R_{sf}$), and (c) charge transfer resistance ($R_{ct}$) as function of discharge potential.

Fig. 7. The Nyquist plots of Ni/NiO anode at (a) 50% DOD and (b) 90% DOD after various cycles. The inset shows the Nyquist plots of the high-frequency range at high magnification.
voltage plateaus, which was mainly due to the nanosized character of the electroproduced particles that generated many new indefinite interfaces [35]. However, one complete conclusion on the mechanism of kinetics change simply with EIS analysis cannot be made, and in the future, more evidence of in-situ characterization methods, such as in-situ XRD and XPS, need to be done [31,32]. But those are beyond the interests and focus of this study.

3.4. Impedance of charge–discharge cycles

The repeating Li-ion conversion reaction upon the cyclic process is another important factor to change the electrode/electrolyte interface. Fig. 7(a) and (b) show the Nyquist plots at the discharge potential of 1.1 V and 0.2 V (50% DOD and 90% DOD) after the indicated number of cycles, respectively. As shown in Fig. 7, all Nyquist plots hold the similar features as illustrated in Fig. 5. It is worth to note that the boundary between the HFS and MFS showed more distinct with increasing cycles. In other words, an overlap depressed semicircle was divided into two independent series semicircles. In fact, this phenomenon had already occurred when the working electrode was operated after 10 cycles. Furthermore, by fitting the impedance data using the equivalent circuit in Fig. 3, the changes in resistance parameters of both DODs during 65 cycles are shown in Fig. 8. The values of $R_s$, $R_{sf}$, and $R_{ct}$ for both DODs displayed identical variation tendency. As shown in the Fig. 8(a), the $R_s$ decreased obviously during the first 30 cycles, and then kept in a relatively stable value in following cycles. This can be mainly attributed to the unique porous core–shell structure of the obtained Ni/NiO electrode experiencing a slow activation process. Interestingly, the charge transfer $R_s$ decreased dramatically during the first 30 cycles (Fig. 8(c)) that agreed well with the change trend of $R_s$ and then gradually increased until 65 cycles. However, an abrupt change of $R_s$ in the 10th cycle can also be found, which may be due to some formed cracks in the thin film electrode, leading to the formation of new SEI layer on the fresh section [32,36]. In particular, this abrupt change exhibited more obvious when the discharge depth increased from 50% to 90%, which can be ascribed to the large volume expansion originating from more complete conversion-reaction at high DOD. This result can be further confirmed by the significant increase of $R_s$ at 90% DOD in the 10th cycle (Fig. 8(b)). In the case of $R_{sf}$, the value almost continued to increase during the charge–discharge cycles, indicating the slow growth of the SEI film on the electrode surface, which is in good consistent with previous studies [19,22,32].

In comparison to the evolution trends of $R_s$, $R_{sf}$, and $R_{ct}$ shown in Fig. 8 with the Coulombic efficiency shown in Fig. 2, it can be concluded that the long term degradation of the obtained Ni/NiO electrode was mainly due to the slow growth of the surface passive layer. More importantly, the effect exhibited more significant when the working electrode was measured over 30 cycles since the values of $R_s$ and $R_{ct}$ were almost constant after 30 cycles. Moreover, the slow increase of $R_{ct}$ indicated the tardy capacity fading of the tested electrode, and thus demonstrated the high capacity retention of the obtained Ni/NiO electrode (Fig. 2).

Based on the aforementioned discussion and results, some significant perspective can be pointed out to further fulfill the performance improvement of transition metal oxide anodes for lithium ion batteries. Firstly, to establish an excellent conductive network for the working electrode is of importance to effectively improve the utilization efficiency of the active material to reduce irreversible capacity loss [37,38]. Secondly, the design and fabrication of porous, hollow, and hierarchical structures is favorable for enhancing the electrode kinetics since large electrode surface area can facilitate the charge transfer on solid/electrolyte interfaces and reduce the resultant impedance [39]. Last but not least, the formation of stable and persistent SEI on the electrode surface can prevent the destruction of active material from the electrolyte, and improve the cyclability of the electrode [30]. As a result, a conductive polymer coating deposited on surface of active material can be considered as a particularly effective method to improve the electrochemical performance of the conversion–reaction type materials [40,41]. Highly conducting polymer can not only improve electronic conductivity of the active material but also inhibit the formation of SEI film to maintain the structural stability of the active material.

4. Conclusions

In this work, we for the first time employed EIS technique to study the relation between the structure/morphology and electrochemical performance of the obtained Ni/NiO anode. It is confirmed that the designed porous core–shell structured Ni/NiO anodes can deliver 701 mAh g$^{-1}$ in the 2nd cycle, and remain at about 646 mAh g$^{-1}$ after 65 cycles with superior capacity retention. In particular, a suitable equivalent circuit based on this binder-free electrode was utilized to investigate the reaction kinetics of NiO anode. It was found that the change of charge transfer resistance is the main contribution to the total resistance change upon cycling. The increase of internal resistance reducing the utilization efficiency of the active material may be a convincing factor to increase the irreversible capacity in the first cycle. The nanosized character of the electroproduced particles that generated many new indefinite interfaces could be the main reason that the well-defined plateau observed during the first discharge vanished on subsequent discharges. Importantly, it was demonstrated that the long term degradation of the obtained Ni/NiO electrode is mainly due to the slow growth of the surface passive layer. Based on the obtained evidences, the possible strategies to optimize the electrochemical performance of transition metal oxide anode materials were proposed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.02.178.

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