Ni-coated Si microchannel plate electrodes in three-dimensional lithium-ion battery anodes

Fei Wang, Shaohui Xu, Shanshan Zhu, Hui Peng, Rong Huang, Lianwei Wang, Xiaohua Xie, Paul K. Chu

A three-dimensional (3D) anode comprising a Ni-coated Si microchannel plate (Si-MCP) as the matrix and active materials is prepared by photo-assisted electrochemical etching and electroless deposition. The morphology of the Ni-coated Si-MCP electrode is characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Using lithium foils as the counter electrodes, representative half-cells are fabricated and tested. Galvanostatic charge–discharge (C–D) measurements are conducted between 0.05 and 1.5 V and the Ni/Si-MCP anode exhibits a charge capacity of 3520 mAh g⁻¹ with a coulombic efficiency close to 95.8% in the initial cycle and above 97% in the second cycle. When the C–D current is stepped up by 25 mAh g⁻¹ every 10 cycles, the capacity always reaches the designed one of 1000 mAh g⁻¹ until the current reaches 100 mAh g⁻¹. Based on electrochemical impedance spectroscopy (EIS) data, the mechanism is studied and described.

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1. Introduction

Lithium-ion batteries are used in various electric devices such as laptop computers and cellular phones as power sources. However, miniaturization of portable devices needs a battery with a smaller footprint area while not compromising the energy density and current capability. Among the various architectures and technologies, three-dimensional battery architectures with high-aspect-ratios are potentially useful [1,2]. Compared to two-dimensional (2D) thin-film batteries, 3D batteries offer a higher energy density for the same footprint and enable shorter diffusion for lithium ions [2]. There have been recent research activities on 3D lithium-ion batteries anodes including nanowires [3–5], porous architectures [6–12], and others [13–16]. Although some architectures deliver outstanding electrochemical performance in half-cell measurements, they may not be suitable for 3D full batteries such as all-solid-state 3D lithium-ion microbatteries [1] because uniform and steady electrode compatible with device processing is imperative.

In this work, a silicon microchannel plate (Si-MCP) is produced as the anode in a Li-ion battery. Compared to the aforementioned 3D structures, the Si-MCP with uniformly vertically aligned arrays and symmetrical structure may constitute a more stable electrode in 3D full batteries. Golodnitsky et al. [17] have prepared 3D electrodes suitable for 3D full batteries with the SiO₂-MCP as the matrix. However, in their electrode design, the SiO₂-MCP is used as only the matrix instead of the active materials. In contrary, with regard the anode described here, besides being the matrix, the Si-MCP also serves as the active materials because silicon has a moderate electrochemical potential versus Li/Li⁺ and high theoretical insertion capacity (4200 mAh g⁻¹ for Li₂Si₅ alloy) [18,19] in a lithium-ion battery. Moreover, the porous structure of the MCP provides sufficient space to accommodate the large volume changes in Si during cycling. In this work, the electrochemical properties of Ni-coated Si-MCP as the anode in a lithium-ion battery are investigated systematically.

2. Experimental

2.1. Silicon MCP preparation

A 100 mm diameter, p-type, (1 0 0), 4–7 Ω cm silicon wafer with a thickness of 520 μm was used in our experiments. A silicon dioxide layer (300 nm thick) was formed by thermal oxidation as the masking layer. After a standard photolithographic process and wet etching in a buffered hydrofluoric acid, the oxide layer was patterned. The patterned wafer was pre-etched in a 25 wt% tetrakis-(dimethylamino)phenylsilane (TMAH) aqueous solution at 85 °C to form the pits with a shape of an inverted pyramid. After anodization
in the photo-assisted electrochemical etching system, the Si-MCP was formed [20,21]. The depth of the Si-MCP pore was about 200 μm and most of the side walls had a thickness of about 1.5 μm. The two ends were a little thinner and the space between two contiguous walls varied from 5.7 μm at the two ends to about 5 μm in the intermediate region. The details are illustrated in Figs. 1 and 2.

### 2.2. Electrode preparation

The electrochemically etched Si-MCP was cut into circular samples 10 mm in diameter for Ni deposition. To enhance adhesion between the Ni layer and silicon surface, the sample was treated in a solution composed of 40 wt% hydrofluoric acid, ethanol, deionized water, and Triton (X-100 = 130:70:100:2, V:V) for 5 min. Electroless deposition of Ni was carried out in the mixture of 0.3 mol L⁻¹ NiCl₂·6H₂O (nickel chloride hexahydrate), 0.1 mol L⁻¹ NH₄Cl (ammonium chloride), 0.1 mol L⁻¹ NaH₂PO₂·H₂O (sodium hypophosphate monohydrate), and 0.02 mol L⁻¹ NaC₂H₃SO₄ (sodium dodecyl sulfate) at 85 °C for 15 min. NiCl₂·6H₂O was used as the Ni ion source, NH₄Cl as the buffering agent, NaH₂PO₂·H₂O as the complexing agent, and NaC₂H₃SO₄ as the stabilizing agent. The pH was adjusted to 8.5 by addition of ammonia. After electroless deposition, the samples were dried at 80 °C for 12 h and to protect Ni from oxidation, the process was carried out under vacuum. The XRD patterns were obtained by Cu Kα radiation.

### 2.3. Coin-cell preparation

Typical CR2025 lithium-ion coin cells were fabricated in an Ar-filled glove box. For comparison, the bare Si-MCP anode was also introduced. In this cell, the bare Si-MCP or Ni/Si-MCP was the working electrode, and a lithium foil which was separated from the working electrode by a porous polypropylene separator (Celgard 3401) acted as the counter electrode. The electrolyte was 1.0 mol L⁻¹ LiPF₆ in ethylene carbonate (EC):diethyl carbonate (DEC):dimethyl carbonate (DMC) (1:1:1, W:W). The potentials were all versus Li⁺/Li unless specially mentioned.

### 2.4. Charge–discharge (C–D) and electrochemical measurements

Several galvanostatic C–D cycle tests under different conditions were employed to investigate the reversibility of the bare Si-MCP or Ni/Si-MCP anode. The cyclic voltammetry (CV) measurement was carried out between the initial open circuit voltage (OCV) and 0.01 V at the first cycle, and then between 1.0 V and 0.01 V for the following cycles at a scanning rate of 0.01 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out from 50 kHz to 0.01 Hz at several potentials during the first insertion. Before each EIS measurement, the cell was equilibrated for 8 h and the corresponding OCV values are shown in Table 1.

### 3. Results and discussion

#### 3.1. Characterization of the Ni/Si-MCP electrode

Figs. 1 and 2 depict the SEM images of the Ni/Si-MCP formed by electroless deposition. Fig. 1 shows the SEM images of the two ends of the Ni/Si-MCP and Fig. 2 displays the images of the intermediate part. The surface and side-walls of the Si-MCP are coated by nickel particles. As shown in Figs. 1(b) and 2, the wall thickness of Si-MCP was about 2 μm, and the thickness of the nickel layer was about 1 μm.

The XRD pattern of the nickel coated Si-MCP is shown in Fig. 3. In addition to the silicon substrate peak Si (4 0 0), the Ni coating was indicated by the presence of the (1 1 1) peaks at 2θ of about 44.2°, 200 at about 51.9°, and (2 2 0) at about 76.4°. The deposited Ni had a face-center-cubic structure [22].

#### 3.2. Performance of C–D cycles

Fig. 4 shows the results of the C–D cycle tests conducted on the bare Si-MCP and Ni/Si-MCP electrodes. When Li alloys with silicon in the first cycle, the voltage drops quickly to 0.2 V and stabilizes at about 0.1 V corresponding to lithiation of the Si-MCP. Limthongkul et al. [23] have found that this flat voltage plateau at 0.1 V from crystalline Si suggests a two-phase field of the constant lithium chemical potential and there is co-existence of crystalline Si and the metastable amorphous phase. During the discharge process, a
Table 1
Fitting parameters for the equivalent circuits for the bare Si-MCP and Ni/Si-MCP anodes.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Charge depths (mAh g(^{-1}))</th>
<th>OCV (V)</th>
<th>(R_0) (Ω)</th>
<th>(R_1) (Ω)</th>
<th>(R_2) (Ω)</th>
<th>(R_3) (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-coated Si-MCP</td>
<td>0</td>
<td>2.271</td>
<td>3.01</td>
<td>0</td>
<td>295</td>
<td>2.7E5</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.176</td>
<td>2.75</td>
<td>148</td>
<td>305</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>0.159</td>
<td>2.95</td>
<td>124</td>
<td>183</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2950</td>
<td>0.100</td>
<td>2.53</td>
<td>108</td>
<td>108</td>
<td>–</td>
</tr>
<tr>
<td>Bare Si-MCP</td>
<td>0</td>
<td>2.725</td>
<td>3.29</td>
<td>0</td>
<td>3300</td>
<td>2.2E6</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.172</td>
<td>2.97</td>
<td>215</td>
<td>140</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>0.147</td>
<td>2.99</td>
<td>138</td>
<td>64</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>2950</td>
<td>0.136</td>
<td>2.75</td>
<td>142</td>
<td>72</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 4. Galvanostatic C–D profiles for (a) bare Si-MCP and (b) Ni/Si-MCP anodes at current density 25 mA g\(^{-1}\) between 0.05 V and 1.5 V.

A rapid increase in voltage is observed, followed by a plateau between 0.3 and 0.5 V. The silicon anodes are thus suitable for Li-ion cells for its operation in such a narrow potential range.

A comparative cycling test for electrodes prepared with bare Si-MCP and Ni/Si-MCP is carried out. The current is set at 10 mA g\(^{-1}\) (C/400, 1 C corresponding to 4000 mA g\(^{-1}\)) for the initial cycle and 25 mA g\(^{-1}\) (C/160) in the latter cycles. As shown in Fig. 4(a), during the initial cycle, the bare Si-MCP anode has a charge capacity of above 3520 mAh g\(^{-1}\) and a discharge capacity close to 2659 mAh g\(^{-1}\), corresponding to a coulombic efficiency of 75.5%. In the second cycle, the discharge capacity is 1128 mAh g\(^{-1}\) with a coulombic efficiency of only 43.9%. Moreover, the discharge curves of the bare Si-MCP anode are quite rough and the potential is unstable above 0.4 V. It may be related to the huge polarization caused by the bad conductivity of bare Si-MCP and the detailed mechanism is being investigated.

Meanwhile, the initial charge capacity of the anode with the Ni coating shown in Fig. 4(b) is 3016 mAh g\(^{-1}\), but the discharge capacity is close to 2890 mAh g\(^{-1}\) with a coulombic efficiency of 95.8%. Even in the second cycle, the coulombic efficiency is still above 97%. As shown in Fig. 5(a), the capacities of both electrodes degrade to below 300 mAh g\(^{-1}\) after 30 cycles. However, the curve of the electrode with the Ni coating descends more gently than the other one. The Ni/Si-MCP anode retains the reversible discharge capacity of above 1000 mAh g\(^{-1}\) until the 19th cycle, while that of the bare Si-MCP anode just stands for the first 2 cycles. It can be explained by that in lithiation and delithiation, the large volume change in the entire Si-MCP electrode structure can introduce and particles with bad electrical contact reduce the amount of active silicon. In contrast, the Ni-coated Si-MCP makes better contact via the Ni layer and it is consistent with the results of EIS measurement.

The Ni coating has an obvious effect in improving the reversible capacity, but the number of available cycle is still not satisfactory. Therefore, a test with a designed capacity of 1500 mAh g\(^{-1}\) in the initial cycle and 1000 mAh g\(^{-1}\) in subsequent cycles between 0.05 V and 1.5 V is performed. Here, charging or discharging in one cycle is continuous until the capacity has reached the designed value or the corresponding cutoff voltage (0.05 V or 1.5 V) has been reached. As shown in Fig. 5, with the current being stepped up by 25 mA g\(^{-1}\) every 10 cycles, the capacity always reaches the designed value

Fig. 5. Capacity vs. cycle number for (a) bare Si-MCP and Ni/Si-MCP anodes at current density 25 mA g\(^{-1}\) between 0.05 V and 1.5 V. (b) Ni/Si-MCP anodes at a designed capacity of 1000 mAh g\(^{-1}\) between 0.05 V and 1.5 V.
until the current reaches 100 mA g\(^{-1}\) (C/40). Compared our results to those reported by Sun et al. [12], it can be found that the more Li alloys with Si, the larger is the volume expansion and this will lead to more significant structural deformation. Therefore, the cycling performance can be improved by limiting the lithiation depth to an appropriate level.

3.3. Electrochemical characterization

The CVs of the first three cycles obtained from the bare Si-MCP and Ni/Si-MCP anodes are shown in Fig. 6. Li insertion occurs mostly at a potential below 0.3 V. In the initial cycle for both electrodes, the reduction current increases sharply below 0.1 V. The peaks at about 0.2 V that appear in the two later cycles do not occur in this cycle. However, during delithiation, there are two oxidation peaks at about 0.36 V and 0.51 V. A similar behavior can also be observed from the CV curves of the Si-MCP electrode in Fig. 7.

According to the results of Si thin films [23–25], this phenomenon can be attributed to the transformation of multiple phases during lithiation and delithiation. During lithiation, the Si structure changes from a crystalline one to a disordered phase, i.e., crystalline silicon structure gradually breaking down into amorphous Si–Li phases. Considering the Ni/Si-MCP anode as an example, the schematic diagram is shown in Fig. 8. During amorphization of Si, there is coexistence of an amorphous surface layer with a central core of crystalline Si [20,26] and for the different insertion levels, there are multiple Li-Si phases (Li\(_x\)Si). During initial lithium insertion, the transformation from the originally continuous crystalline region to an amorphous phase plays a dominant role. Therefore, the region between 0 and 0.1 V during the course of lithiation in fact should be a region in which multiple phases coexist. It also explains the two oxidation peaks at about 0.36 V and 0.51 V during delithiation.

Owing to the formation of the amorphous Si–Li phase, diffusion of Li ions becomes easier and it may explain why the peaks of both electrodes become more distinct in the first three cycles. It is slightly different that the peaks at about 0.51 V for the bare Si-MCP electrode becomes indistinct in the last two cycles. This can be attributed to the breakdown of the amorphous surface layer during delithiation. All these observations are consistent with the C–D cycle test results.

The impedance features in terms of the Nyquist plots for first lithiation and corresponding equivalent circuits are exhibited in Figs. 9 and 10 and the corresponding circuit parameters are listed in Table 1.

For the bare Si-MCP electrode at 0 mAh g\(^{-1}\), as shown in Fig. 9(a), the spectra consist of a quarter circle at high frequencies but distinct circular arc at low frequencies. Similar to the EIS analysis of silicon nanowires [27], the spectra at frequencies above 10 kHz are dominated by connections including the external cell connections, electronic conduction between the substrate and active materials, and ionic conduction through the electrolyte. In our circuit model, the resistor \(R_0\) is used to simulate this pure resistive behavior. Moreover, the changes in \(R_0\) in lithiation of Si are not obvious.

The semicircle between 10 kHz and 20 Hz can be simulated by a resistor \(R_1\) in parallel with the double layer capacitance \(C_1\), where \(R_1\) may be ascribed to the presence of the solid electrolyte interface (SEI) layer [27]. A constant phase-angle element (CPE) named \(Q_1\) is introduced to replace \(C_1\). The CPE element arises from the porous nature of the electrode [28]. Owing to the absence of the SEI at OCV, \(R_1\) in this stage is equal to 0 \(\Omega\) as shown in Table 1. Therefore, this depressed semicircle between 10 kHz and 20 Hz can only stem from charge transfer. Another CPE named \(Q_2\) in parallel with resistor \(R_2\) is employed to simulate the charge transfer behavior. By comparing
the values of $R_2$ for both anodes and as shown in Table 1, $R_2$ for the Ni/Si-MCP anode is much smaller. That is, the Ni coating benefits charge transfer.

The impedance between 20 Hz and 1 Hz should be attributed to diffusion of Li ions from the reaction interface into the bulk of Si-MCP and it is fitted by the Warburg impedance $W_0$. The circular arc below 1 Hz is related to the change in the crystalline structure [29], that is, transformation from crystalline Si to amorphous Li$_x$Si phases. Therefore, a CPE named $Q_3$ in parallel with a resistor $R_3$ is used to simulate this process.

![Fig. 9. Impedance measurements and equivalent circuits for (a) bare Si and (b) Ni/Si-MCP anodes at the charging depth of 0 mAh g$^{-1}$.

![Fig. 10. Impedance measurements and equivalent circuits for (I) bare Si and (II) Ni/Si-MCP anodes, respectively, at (a) 350 mAh g$^{-1}$, (b) 1050 mAh g$^{-1}$, and (c) 2950 mAh g$^{-1}$.

As the charge depth drops to 350 mAh g$^{-1}$, the impedance spectrum changes a lot. Besides a depressed semicircle between 20 Hz and 0.1 Hz, a new one emerges from the intermediate-frequency region between 10 kHz and 20 Hz. This depressed semicircle stems from charge transfer. However, the circular arc corresponding to the transformation of phases in the 0 mAh g$^{-1}$ can no longer be detected. A possible interpretation is that the corresponding circular arc may go beyond 0.01 Hz. The spectra at 1050 mAh g$^{-1}$ and 2950 mAh g$^{-1}$ are similar to that at 350 mAh g$^{-1}$. Therefore, it is reasonable to use the same equivalent circuit for fitting. Regarding the SEI layer, the change in R1 is not discussed here because the distance between 0 mAh g$^{-1}$ and 1050 mAh g$^{-1}$ is too long to be representative. Moreover, the purpose of our EIS tests is to investigate the roles played by the Ni coating.

Compared to that at 0 mAh g$^{-1}$, R2 at 350 mAh g$^{-1}$ decreases by more than 90%, indicating that charge transfer becomes easier. Because formation of the Li$_x$Si layer results increases the conductivity, charge transfer is facilitated. With lithiation of Si to a deep level, the resistance of the charge transfer increases, e.g., R2 at 2950 mAh g$^{-1}$ being bigger than that at 1050 mAh g$^{-1}$. It is because of the larger thickness of the Li$_x$Si layer which increases the difficulty for charge transfer [26].

The same equivalent circuits used for the bare Si-MCP electrode are also suitable for the Ni/Si-MCP. For the Ni/Si-MCP electrode, R2 at the charge level of 0 mAh g$^{-1}$ is 295 $\Omega$, which is almost the same as the one at 350 mAh g$^{-1}$. With increase Li contents, R2 decreases gradually to 108 $\Omega$ at 2950 mAh g$^{-1}$. Compared to the bare Si-MCP electrode, the charge in R2 illustrates the advantage of the Ni coating which improves the conductivity and promotes charge transfer especially in the early stage of lithiation.

4. Conclusion

A 3D lithium-ion battery anode is successfully fabricated using a Si-MCP with a Ni coating. Compared to the anode without the Ni coating, the Ni/Si-MCP anode exhibits better cycle performance in the galvanostatic half-cell measurements. The excellent performance is ascribed to the existence of the Ni coating which greatly improves the conductivity and promotes charge transfer especially in the early stage of lithiation. In addition, fabrication of the Si-MCP array is compatible with conventional integrated circuit (IC) processing thereby enabling incorporation of this 3D lithium-ion battery structure into commercial devices.

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