



Short communication

## Electrochemical behaviors of wax-coated Li powder/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells

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## ABSTRACT

The wax-coated Li powder specimen was effectively synthesized using the drop emulsion technique (DET). The wax layer on the powder was verified by SEM, Focused Ion Beam (FIB), EDX and XPS. The porosity of a sintered wax-coated Li electrode was measured by linear sweep voltammetry (LSV) and compared with that of a bare, i.e., un-coated Li electrode. The electrochemical behavior of the wax-coated Li powder anode cell was examined by the impedance analysis and cyclic testing methods. The cyclic behavior of the wax-coated Li powder anode with the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) cathode cell was examined at a constant current density of  $0.35 \text{ mA cm}^{-2}$  with the cut-off voltages of 1.2–2.0 V at 25 °C. Over 90% of the initial capacity of the cell remained even after the 300th cycle. The wax-coated Li powder was confirmed to be a stable anode material.

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### 1. Introduction

The lithium metal is an attractive material for use as a negative electrode in rechargeable batteries because it has high theoretical capacity. Concerns over dendritic deposition of lithium metal, however, have prevented its use in rechargeable batteries [1,2]. In order to suppress dendritic deposition, many researchers have attempted to modify the morphology and properties of the surface film on lithium [3].

To overcome propensity toward dendritic deposition, the compacted lithium powder instead of the lithium bulk foil has recently been suggested as a new anode material. The cycling efficiency of the lithium powder electrode has remarkably improved over that of the lithium foil electrode [4]. Solid electrolyte interface (SEI) controls on the lithium powder also demonstrated that the electrochemical properties and safety of the lithium powder cell can be improved [3,5,6]. In the present study, wax (Degussa, Germany) was used as an SEI control agent for the lithium powder. An effective SEI layer is the result of a rapid formation  $\text{Li}^+$  ion conducting and electrochemically insulating products to completely cover the electrode surface [7]. A series of tests evaluated the performance of the wax-coated lithium powder as an electrode and as a full cell by creating a cell using  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) as a counter electrode.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  was used as a counter electrode because it is known to remain a stable electrode (in this case, a cathode) for over 100 charge/discharge cycles. Moreover,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is appropriate for evaluating the performance

since it cannot act as a  $\text{Li}^+$  source and has a spinel structure that does not change even after 100 cycles have elapsed [8]. The two main goals of the present study were to develop a wax-coating technique on the Li powder and to gain understanding of the electrochemical and cyclic properties of the wax-coated Li powder anode cell.

### 2. Experimental

#### 2.1. Preparation of the wax-coated lithium powder specimen

The lithium powder specimens were safely produced by applying the drop emulsion technique (DET) process. Solid wax was added into silicon oil during the process. Since liquid lithium is emulsified during the DET process, the surface of the lithium is exposed to the silicon oil. Through the addition of a surfactant to the silicon oil, the surface film on the lithium powder can be modified through the interaction of the surfactant with the bare surface of lithium [9]. The wax melted and coated the lithium droplets during the powder making process. The presence of the wax film on the lithium powder was verified by FE-SEM (Hitachi, S-4700), Focused Ion Beam (FIB), EDX mapping (FEI company, Nova 200) and XPS.

#### 2.2. Measurements

The coin cell (CR 2032) was assembled in an Ar-filled glove box. The electrolyte used was 1 M LiPF<sub>6</sub> with the volume ratio of 1:1:1 for ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (from Techno Semichem), respectively.

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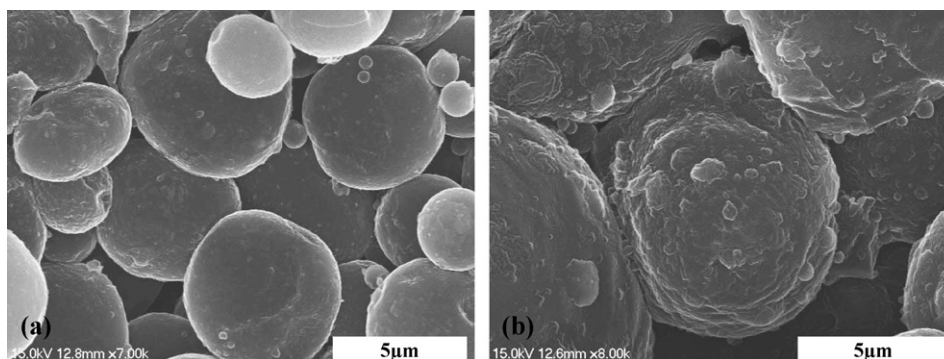


Fig. 1. SEM images of (a) lithium powder and (b) wax-coated lithium powder.

For this test, two types of cells were used. The first cell type used the lithium foil as a counter electrode and subjected it to the impedance analysis. It was also used to measure the porosity of the compacted electrode by linear sweep voltammetry (LSV) analysis. The impedance analyzer (Solartron, SI 1255) was operated by an alternating current voltage with the frequency range of 100 MHz to 100 kHz and the magnitude of 5 mV. In the case of LSV, the potential was set at 0–0.02 V while the scan rate was set at  $0.1 \text{ mV s}^{-1}$ . The second type cell used  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as a cathode. The cathode consisted of 90%  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , 2% super P and 8% PVDF as a binder. The wax-coated Li powder/LTO cell was subjected to charging/discharging tests, which was performed galvanostatically at a constant current density of  $0.35 \text{ mA cm}^{-2}$  with the cut-off voltages of 1.2–2.0 V at  $25^\circ\text{C}$ . The electrochemical behavior of the wax-coated lithium powder/LTO cell was also analyzed by a cycler (Wonatech 3000).

### 3. Results and discussion

#### 3.1. Verification of the wax layer

The FE-SEM analysis was conducted to compare the morphology of the lithium powder and the wax-coated lithium powder, as shown in Fig. 1. It was found that (a) the surface of the lithium powder is smooth and (b) the surface of the wax-coated lithium powder is rough. This finding confirms that a wax layer coats the surface of the lithium powder. The wax-coated powder is slightly larger than the lithium powder because the addition of wax during the powder synthesis increases the viscosity of the carrier fluid (silicon oil). The increased viscosity of silicon oil decreases the rotation speed of the impeller which in turn reduces the shear force. The rotation of the impeller controls the particle size of the powder during the DET

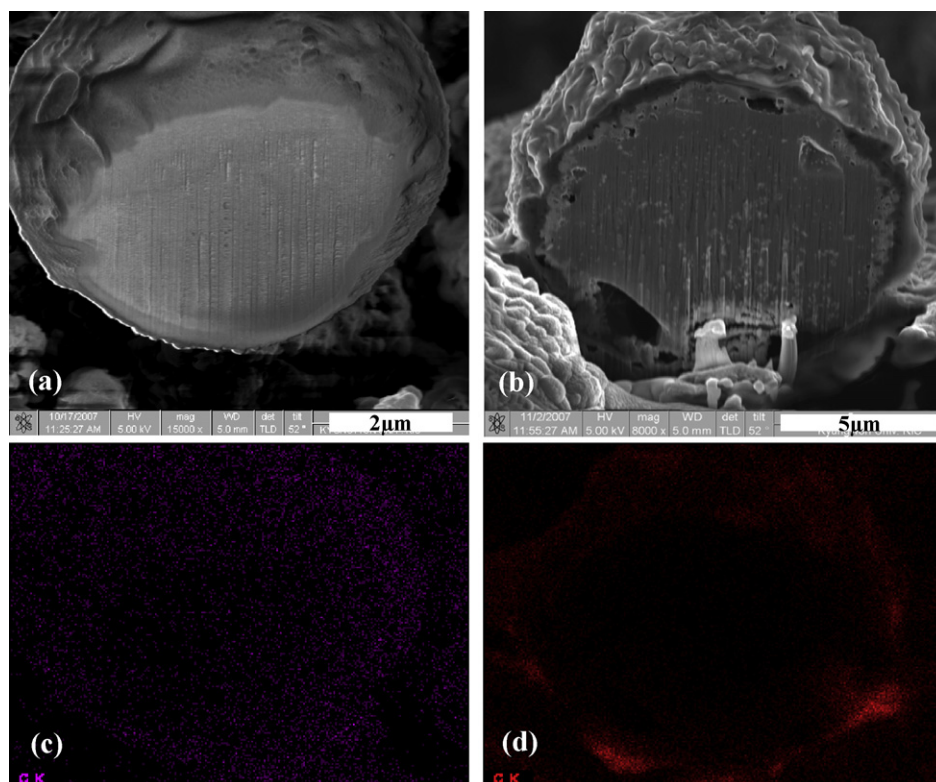


Fig. 2. The cross-section of (a) lithium powder, (b) wax-coated lithium powder by Focused Ion Beam. The carbon mapping of (c) lithium powder, (d) wax-coated lithium powder by EDX.

manufacturing process, and the decreased rotation speed increases the size of the powder [10].

A FIB cross-sectional image of the Li powder with a waxed surface layer is shown in Fig. 2(b). The image shows that the Li powder is encased in a wax film. For comparison, a cross-sectional image of the un-coated Li powder is shown in Fig. 2(a). Fig. 2(c) and (d) shows the carbon mapping by EDX of the un-coated powder and wax-coated powder cases, respectively. Since the wax material mainly consists of the carbon, in the case of the wax-coated powder, carbon is present mainly in the wax film, as expected. On the other hand, the carbon appears to be uniformly distributed in the case of the un-coated Li powder due to the presence of carbonates such as  $\text{Li}_2\text{CO}_3$  which is formed by a reaction between Li and  $\text{CO}_2$  in the atmosphere. Therefore, EDX and FIB images confirm the existence of the wax surface layer.

Fig. 3 shows the XPS results of (a) the lithium powder and (b) the wax-coated lithium powder. Fig. 3(c) shows that after 3 and 1/2 min following the application of Ar gas, a lithium peak corresponding to the binding energy of 56 eV is observed in the case of the lithium

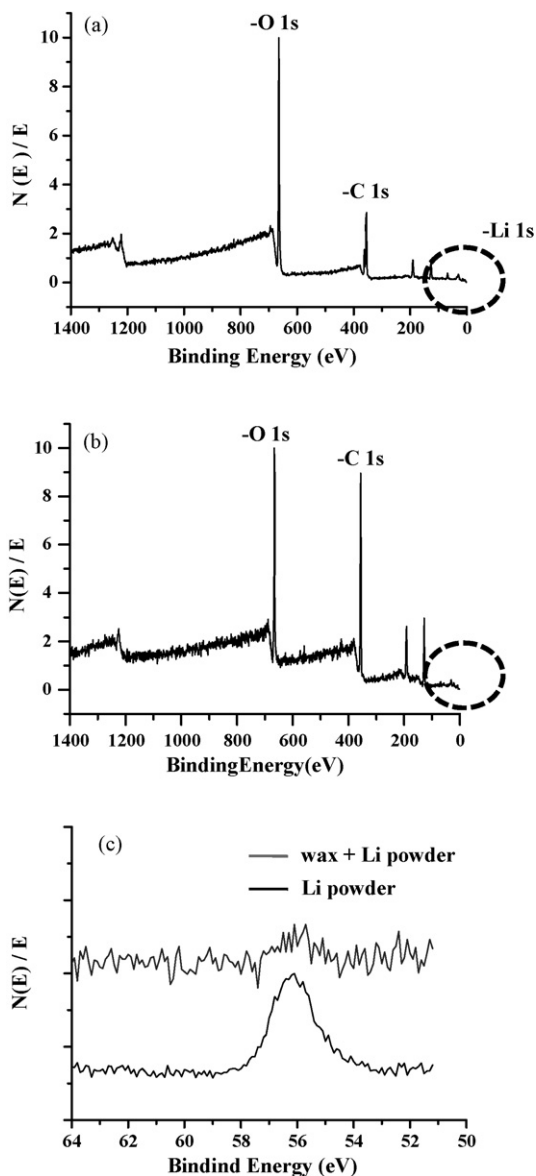


Fig. 3. XPS spectra of (a) lithium powder, (b) wax-coated lithium powder and (c) lithium peak of (a), (b).

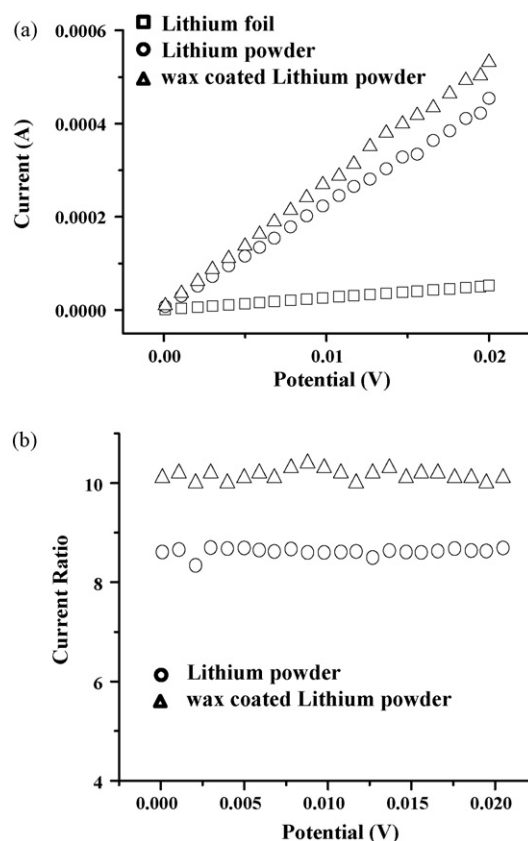


Fig. 4. LSV analysis for (a) lithium foil, lithium powder and wax-coated lithium powder (b) current ratio of lithium powder and wax-coated lithium powder from lithium foil.

powder. However, no peak is observed in the case of the wax-coated lithium powder. This finding confirms that the lithium powder has been coated with wax.

### 3.2. Electrochemical properties

LSV method denotes a voltammetric method for experimental study of the electrochemical reaction: By measuring the value of the current flowing into the cell as the voltage is applied, the LSV method has been reported to furnish fairly reliable estimate of the total area of the reacting areas that participate in the electrochemical reaction [11,12]. For porous electrodes, the reacting area is commonly estimated by measuring the value of current due to low applied voltage (0–0.02 V) existing during an initial stage of the experiment. The area estimated by LSV method in this manner is found to be close in value to the area more directly measured by applying the well-known Brunauer–Emmett–Teller (BET) method [13].

Fig. 4(a) shows the LSV data for cells with electrodes made of Li foil, Li powder and wax-coated Li powder at one end respectively and with a counter electrode made of lithium foil at the other end. Li powder electrode as well as wax-coated Li powder electrode releases much greater current than that of Li foil electrode. Fig. 4(b) shows the current ratios, i.e., the ratios of the active surface area of Li powder and wax-coated Li powder over that of Li foil, respectively. As an indication of the area of the reaction zones for the 0–0.02 voltage range, lithium powder releases about 8.5 times more current while wax-coated lithium powder releases 10 times more current than that of Li foil. Therefore, it can be inferred that the surface area of wax-coated Li powder electrode is larger than that of Li foil

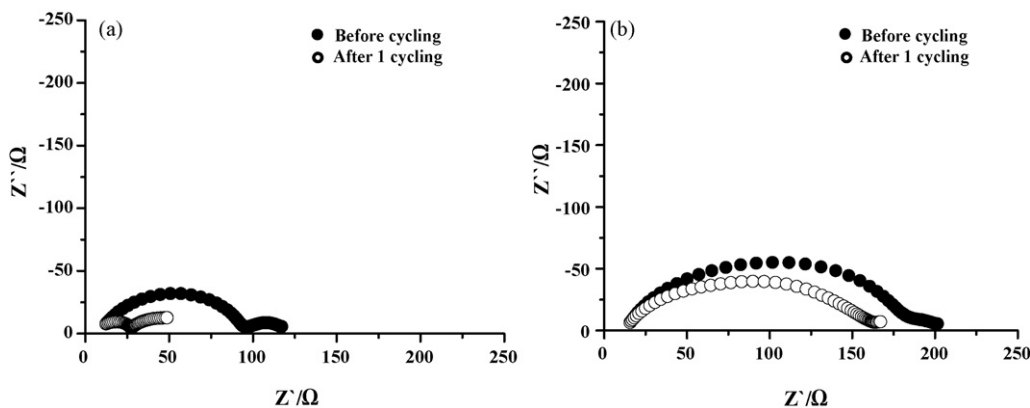


Fig. 5. The impedance analysis at before and after 1 cycling for (a) lithium powder and (b) wax-coated lithium powder.

electrode by a factor of about 10 and that the electrochemical properties of wax-coated Li powder can be attributed to a corresponding increase in the total reacting area.

Fig. 5 shows data on the change in the impedance before and after one charge/discharge cycle. According to Fig. 5(a) and (b), the initial value is greater for the wax-coated lithium powder. However, just after one cycle, the impedance for the wax-coated lithium powder changes by a much smaller value than that of the lithium powder. Here, the wax layer is playing the role of the SEI, and very little change in the internal resistance is taking place even during charging/discharging.

The cyclic performance is shown in Fig. 6. The lithium foil cell displays a capacity of  $121 \text{ mA h g}^{-1}$  for the first cycle at the cut-off voltage of 1.2–2.0 V at  $25^\circ\text{C}$ , which was approximately 80% of theoretical capacity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [8]. The reduced present capacity may be due to current density and experimental cut-off voltage range difference. The capacity of the lithium foil cell begins to decrease from the 90th cycle on and falls to  $28.5 \text{ mA h g}^{-1}$  at the 300th cycle. Dendrites are suppressed more effectively in the lithium powder than in the lithium foil, and Fig. 6 shows that the lithium powder maintains their initial capacity up until the 200th cycle, at which point the capacity begins to decrease and falls to  $28.1 \text{ mA h g}^{-1}$  by the 300th cycle. In contrast, the wax-coated lithium powder has a capacity of  $116 \text{ mA h g}^{-1}$  for the first cycle and maintains approximately 90% of their initial capacity even after the 300th cycle with the capacity given by  $105 \text{ mA h g}^{-1}$ . The present finding means that the wax-

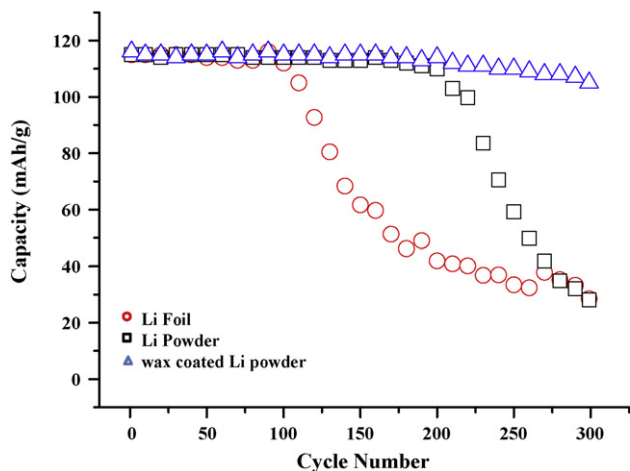


Fig. 6. The cycle performance of Li foil/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , Li powder/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , wax-coated Li powder/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$  cells at 1.2–2.0 V and  $0.35 \text{ mA cm}^{-2}$ .

coated lithium powder exhibits improved cyclic performance as an electrode than both the lithium powder and the lithium foil. The reason for the improved cyclic performance is due to the electro and physical properties of the wax-coated lithium powder. Based on the LSV results, the effective surface area of the compacted wax-coated powder that participates in the charge/discharge reaction is greater than that of both the lithium foil and the lithium powder. Also, due to stable and sound character of the wax coating even after the charge/discharge have repeatedly taken place, the wax layer prevents the lithium powder from reacting with the electrolytes which in turn mitigates the extent of the electrolyte loss.

#### 4. Conclusions

A new technique for wax coating on the Li powder has been developed using the DET method. As verified by SEM, FIB, EDX mapping and XPS, the wax was found to completely cover the Li powder. The wax-coated lithium powder electrode exhibited improved cyclic performance compared with both the un-coated lithium powder and the lithium foil electrode. The wax-coated Li powder/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$  cell was shown to maintain over 90% of the initial capacity for up to the 300th charge/discharge cycle. The improved cyclic performance of the wax-coated Li powder anode cell was due to increased surface area of the electrode as well as the stable character of the wax surface layer on the Li powder.

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#### References

- [1] E. Peled, *J. Electrochem. Soc.* 126 (1979) 2047.
- [2] E. Peled, *Lithium Batteries*, Academic Press, New York, 1983 (Chapter 3).
- [3] S.T. Hong, J.S. Kim, S.J. Lim, W.Y. Yoon, *Electrochem. Acta* 50 (2004) 535–539.
- [4] W.Y. Yoon, J.S. Paik, D. Lacourt, J.H. Perepezko, *J. Appl. Phys.* 60 (1986) 3489.
- [5] S.W. Kim, Y.J. Ahn, W.Y. Yoon, *Electrochem. Acta* 50 (2004) 345.
- [6] J.H. Chung, W.S. Kim, W.Y. Yoon, S.W. Min, B.W. Cho, *J. Power Sources* 163 (2006) 191–195.
- [7] E. Peled, D. Golodnitsky, C. Menachem, D. Bar-tov, *J. Electrochem. Soc.* 145 (1998) 3482.
- [8] J. Gao, C. Jiang, J. Ying, C. Wan, *J. Power Sources* 155 (2006) 364–367.
- [9] K. Kanamura, S. Shiraishi, Z. Takehara, *J. Electrochem. Soc.* 141 (1994) 108.
- [10] J.Y. Kim, W.Y. Yoon, *J. Korean Foundrymen's* 15 (1995) 164.
- [11] X. Zuo, C. Xu, H. Xin, *Electrochim. Acta* 42 (1997) 2555.
- [12] P. Georen, G. Lindbergh, *J. Power Sources* 124 (2003) 213.
- [13] M.S. Park, W.Y. Yoon, *J. Power Sources* 114 (2003) 237.