

# Novel solvent-free direct coating process for battery electrodes and their electrochemical performance

Dong-Won Park<sup>a,\*</sup>, Natalia A. Cañas<sup>a</sup>, Norbert Wagner<sup>a</sup>, and K. Andreas Friedrich<sup>a</sup>

<sup>a</sup>Institute of Engineering Thermodynamics, German Aerospace Center (DLR), 70569 Stuttgart, Germany

## Abstract

We report a novel solvent-free direct coating process for fabricating a well-structured electrode. The manufacturing process was rapid and facile, involving only dry-spraying of the solvent-free electrode component mixture and a subsequent isothermal hot-pressing. The electrochemical and physicochemical properties of the dry-sprayed electrode with hot-pressing were evaluated in order to understand the correlation between a preparation parameter, morphological characteristic of the electrode, and cell performance. The hot-pressing time had an effect on the binder distribution, which in turn resulted in different electrode morphologies and performance. The dry-sprayed LTO electrode prepared at a hot-pressing time of 60 min had excellent electrical conductivity and  $\text{Li}^+$  storage capacity, owing to its electron transport structure, which was more suitable than the prepared electrodes at other hot-pressing conditions.

**Keywords:** Dry-spray coating, solvent-free, battery, LTO

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\*Corresponding author. Tel.: +49 711 6862 8178; fax: +49 711 6862 747.

*E-mail address:* Dong-Won.Park@dlr.de (D.-W. Park)

## 1. Introduction

Due to the need for a transformation of the energy system towards renewable energies which are volatile and fluctuating, many attempts have been made to develop efficient and durable energy storage technologies [1-4]. Among these storage devices, rechargeable lithium-ion batteries (LIBs) with high power and energy density have attracted significant attention from both industry and academia as power sources; LIBs are used as electric vehicles (EVs) and the smart grid system [5-7]. These applications have spurred the development of novel materials and architectures for achieving high energy/power density, long cycle life, and low production cost. Furthermore, recent investigations on LIBs have focused primarily on material design and synthesis, as a means of improving the performance of the electrodes. The electrodes were, however, still fabricated in a conventional manner; i.e., *via* a wet process such as slurry casting.

Electrodes used in LIBs are typically prepared from a viscous slurry of active material (AM) and carbon black (CB), bound together by polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) as a solvent. The slurry is then coated onto the current collector using the doctor-blade method and dried to form the electrode. However, electrodes prepared using this method typically suffer from several drawbacks, namely, i) NMP is harmful to the human reproductive system; ii) the electrical/mechanical contact loss owing to changes in the physicochemical properties of the polymer binder during solvent evaporation reduces the particle/particle and particle/substrate adhesion; and iii) large volume expansion owing to the use of new active materials, such as metal (Me) and metal oxide (MO<sub>x</sub>), which leads to a rapid decrease in the capacity.

To overcome these drawbacks, several approaches have been adopted to optimize the electrode by replacing the solvent and developing advanced binders such as solvent-soluble, water-soluble, and flexible functionalized binders [8-11]. These binders have resulted in some improvements and, hence renewed interest in the correlation between the particles and

polymer, since the binder has a significant effect on the performance of the electrode. However, issues related to the electrode characteristics such as swelling, dispersion, and mechanical strength remains unresolved. The electrode manufacturing process can be changed by avoiding the use of binder's altogether. For example, 1D-3D nanomaterials were recently grown directly on the current collector by using sputtering and chemical vapor deposition (CVD) methods [12-16]. The cell performance of electrodes fabricated by using various methods such as spray coating, electrochemical etching, chemical bath deposition, etc., was also evaluated [17-21]. However, these methods are complicated and time-/energy-consuming, and are therefore unsuitable for the low-cost, mass production of the electrode material as well as large-area electrodes.

Developing a low-cost manufacturing process and high-performance electrode materials is therefore essential to realizing commercially viable mass production. As such, in this paper, we introduce a dry-spray method capable of directly coating dry powder onto the substrate, as an advanced manufacturing process, which is developed at our institute [22-24]. The key features of this method are the ability to (i) achieve excellent contact between the electrode components, thereby avoiding the use of environmentally hazardous solvents and (ii) eliminate the waiting time required for solvent evaporation; this waiting time typically has an adverse effect on the properties of the electrode. The amount of loading and morphology of the electrode can also be controlled, depending on the composition and the surface properties of the raw material powder. Therefore, owing to the short time required to manufacture and scale-up the electrode, we believe that the dry-spraying process has significant potential as an important industrial technique for producing the electrodes of batteries.

Here, we report the first-ever battery electrodes fabricated using the dry-spraying method as a novel solvent-free direct coating process. The performance of the electrode was measured in order to understand the relationship among the components contained therein. In addition,

we used micro-sized commercial  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) as the active material to demonstrate that the dry-spraying method can be used for all electrode materials such as Me,  $\text{MO}_x$ , and carbon.

## 2. Experimental

Prior to dry-spraying, 80 wt.%  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (Aldrich) was evenly mixed with 10 wt.% carbon black (Alfa Aesar) and 10 wt.% PVDF (Alfa Aesar) for 5 min in a double blade mill. The powder mixture was then loaded into a powder feeder connected to a 60-mm-long metal slot. The slot-substrate distance was fixed at 1 cm. In order to obtain a homogeneous layer, the powder mixture was directly sprayed onto the substrate thrice using the dry-spraying machine; an  $\text{N}_2$  gas stream, which flows bi-directionally from the bottom and side, was used during spraying, and the flow rate of  $\text{N}_2$  gas was controlled by flow meter with applying voltages of 1.0 V and 0.1 V. The adhesion of the electrode component material on the substrate seemed adequate (Figure S1). However, the as-dry-sprayed LTO electrode was isothermally hot-pressed at 175 °C, under a pressure  $6 \text{ kg}\cdot\text{cm}^{-2}$ , for various times in order to enhance the mechanical and electrical contact. The electrode manufacturing process via dry-spraying is schematically shown in Fig. 1. The final dry-sprayed LTO (DS-LTO) electrode prepared by hot-pressing for 30, 45, 60, and 90 min are referred to as DS-LTO-30, DS-LTO-45, DS-LTO-60, and DS-LTO-90, respectively.

A lithium metal foil (12 mm in diameter, Aldrich), a 25- $\mu\text{m}$ -thick porous polymer membrane (Celgard 2500), and 1 M  $\text{LiPF}_6$ , EC:DMC (1:1, v/v) were used as the respective counter electrode, separator, and electrolyte in the Swagelok cells. The cells were assembled in an Ar-filled glove box. Moreover, a battery test system (BaSyTec XCTS) was used to measure the galvanostatic charge/discharge properties at room temperature with voltages of 2.5-1.0 V (vs.  $\text{Li}/\text{Li}^+$ ). Electrochemical impedance spectroscopy (EIS) measurements were performed at frequencies of 100 kHz-10 mHz on an electrochemical workstation (Zahner®

IM6 with Thales battery software). Furthermore, the morphology and structure of the electrodes were examined via scanning electron microscopy (SEM, Zeiss ULTRA plus). The thermal behavior of the LTO electrodes was evaluated by using a thermogravimetric/differential scanning calorimetry (TG/DSC) analyzer (NETZSCH STA 449 C). In addition, Fourier-transform infrared (FTIR) measurements were performed in the transmission mode on samples pressed as KBr pellets; a Bruker Vertex 80v spectrometer equipped with an LN2 cooled mercury-cadmium-telluride (MCT) detector, which allows for analysis over a spectral range of 600-4000  $\text{cm}^{-1}$ , was used for the measurements. The IR light was produced by a water-cooled back body source (Globar) and the spectra were acquired at 2  $\text{cm}^{-1}$  resolution from 20 superimposed scans.

### 3. Results and discussion

The electrochemical performance of the electrodes in the LTO/Li half-cells was characterized. The  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes prepared by hot-pressing (HP) for various times at a fixed temperature were tested, and the initial charge-discharge performance was evaluated at 0.2 C (35  $\text{mA}\cdot\text{g}^{-1}$ ) and potentials of 1.0-2.5 V (*vs.* Li/Li<sup>+</sup>). An HP temperature of 175 °C was used since the PVDF has a melting point of 155-160 °C, according to supplier specifications (Fig. S2). However, the untreated hot-pressed electrodes exhibited no performance at all, since the electrode components became easily detached from main body and collector owing to low adhesion. Therefore, we evaluated a DS-LTO-5 electrode that was hot-pressed for 5 min as the minimum condition for comparison (Fig. 2) with the other electrodes. As the figure shows, the charge/discharge curves exhibit a plateau at ~1.5-1.6 V (*vs.* Li/Li<sup>+</sup>), which is similar to that observed in the conventional micro-sized LTO electrode; this plateau corresponds to the reversible two-phase reaction between  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  [25,26]. The DS-LTO-5 electrode delivered a capacity of 24  $\text{mAh}\cdot\text{g}^{-1}$ . However, the delivered capacity

of DS-LTO electrodes hot-pressed for longer than 30 min increased with increasing HP time; i.e., HP times of 30, 45, and 60 min resulted in capacities of 113, 131, and 162 mAh·g<sup>-1</sup>, respectively. When the HP time was further increased to 90 min, the resulting capacity (127 mAh·g<sup>-1</sup>) was, however, lower than those of the DS-LTO-45 electrodes. This can be attributed to the binding force between the AM and CB particles; i.e., owing to the homogeneous coating of the electrode component material during dry-spraying, the PVDF is melted to different extents depending on the HP time (Fig. S4). Moreover, the binder plays a key role in determining the mechanical strength and electronic conductivity of the electrode [27,28]. The binder plays a similar role to that of the post-heat-treatment of the completed electrode; i.e., an additional heat-treatment at high temperature melts lumps of carbon black-filled PVDF, thereby leading to improved performance [29]. The morphology of the electrode varies therefore with the HP-time-dependent dispersion of the binder, which affects the cell performance.

Figure 3 shows the morphologies of the DS-LTO electrodes prepared at different HP times, and a schematic illustration of the component interaction in the electrode. The SEM images all reveal similar microstructures that are comprised of LTO particles with diameters of 60 nm to 1.5 μm. These particles have a nearly polyhedral-symmetry structural morphology (Fig. S3). Figure 3a shows that the PVDF did not to cover the particles completely. In fact, the carbon black-filled PVDF lumps are especially noticeable in the DS-LTO-30, DS-LTO-45, and DS-LTO-90 electrodes. This may be explained as follows: the PVDF starts to melt as the HP time is increased; the melted PVDF covers the particles and simultaneously permeates the pores between the AM and the CB. The polymer then combines with dangling bonds on the surface of the solid particle, either through chemical bonding or physical adsorption, thereby forming a polymer layer, which has limited mobility; Liu *et al* [28] referred to this layer as a fixed layer. However, owing to the high content of AM, there is insufficient PVDF to form a fixed layer, which completely wraps around both the AM and the CB. Hence, some of the PVDF is

distributed between the AM and the CB, as shown in Fig. 3b. In this case, the CB tends to form a network that promotes electron transfer through the aggregates, and the AM surface is, in turn, surrounded by the CB network. However, the aggregated CB may result in deterioration of the electrode adhesion, thereby reducing the contact area between the particles. Furthermore, if the HP time (thermal energy) is insufficient, the unfixed polymer surrounding the particles acts as a major factor that leads to increased resistance and reduced electrolyte penetration; i.e., the un-melted PVDF in the non-HP and DS-LTO-5 electrodes, acts as a resistance component. The particle/particle (and/or particle/current collector) network in these electrodes is electrically disconnected, thereby resulting in poor cell performance. The DS-LTO electrode resulting from HP times longer than 30 min, exhibits an enhanced melting degree and dispersibility, which results in excellent mechanical strength and electrical conduction. However, at HP times above 90 min, the PVDF shrinks again *via* recrystallization, and the previously dispersed PVDF is re-agglomerated in the electrode; the temperature, time, and pressure dependence of the properties of the PVDF has been shown in several studies [30-32]. **The distribution of the binder polymer in accordance with the HP time can be confirmed through the cross-sectional SEM image of the dry-sprayed electrode, and the surface morphology of PVdF powder shows obvious changes corresponding to HP time (Fig. S4 and S5).** The re-agglomerated PVDF results in a diminished cell performance owing to the electrically disconnected network. The agglomerated or partly melted PVDFs may also hinder the  $\text{Li}^+$  transport as a result of the lengthened pathway and a reduction in the electrode porosity. Consequently,  $\text{Li}^+$  does not react with the AM particles completely, and this incomplete reaction leads to a relatively low capacity. The melting behavior of the polymer binder also results in a change of thickness of the electrode, which may, in turn, affect the cell performance owing to the shortened pathway. Based on these results, we conclude that a well-connected electrode structure is obtained in an HP time of 60 min.

As previously mentioned, the low-mobility fixed polymer layer is difficult to realign, and hence, it contributes partially to melting and crystallization; the thermal physical properties of the DS-LTO electrode were investigated in order to determine the validity of this hypothesis. Figure 4 shows the TG-DSC curves of the DS-LTO-30, DS-LTO-45, DS-LTO-60, and DS-LTO-90 electrodes obtained at a heating rate of  $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  from 30-800  $^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere with a flow rate of  $25\text{ mL}\cdot\text{min}^{-1}$ . As the figure shows, the samples exhibit similar weight loss behavior. The exothermic peaks at temperatures lower than 100  $^{\circ}\text{C}$  are attributed to the vaporization of trace amounts of weakly adsorbed water on the surface of the particle; the samples are all thermally stable up to 250  $^{\circ}\text{C}$  and do not experiences weight loss. The endothermic peak (A) at  $\sim 150\text{ }^{\circ}\text{C}$  is attributed to the melting of the PVDF and is consistent with the specifications of commercial PVDF. There are two obvious weight loss regimes in the TG curves. The first regime, which occurs between 270  $^{\circ}\text{C}$  and 425  $^{\circ}\text{C}$ , results possibly from the decomposition of organic species on the surface of the LTO and carbon black. The second regime, which is observed at temperatures of 425-560  $^{\circ}\text{C}$ , is attributed to the decomposition of the PVDF. Furthermore, the weight is approximately constant at temperatures above 560  $^{\circ}\text{C}$ , corresponding to a residual weight of almost 84% for each sample. Since the DSC is performed at constant pressure, the heat flow is equal to the change in enthalpy, and therefore, the enthalpy of fusion ( $\Delta H_f$ ) is obtained from the area under the melting thermogram [27,29]. We can also estimate the level of adhesion from the change in enthalpy with HP time, the level of adhesion affects the electrode properties. The DS-LTO electrode that was isothermally hot-pressed at 175  $^{\circ}\text{C}$  for various times, exhibited endothermic peaks whose amplitudes decrease with increasing HP time; this indicates that the final product formed is LTO partially combined with the CB via a melted PVDF. The amplitude of the endothermic peak increases at HP times greater than 90 min. This results possibly from the crystallization of increasing amounts of unfixed polymer, which in turn



leads to an increase in the enthalpy of fusion. In addition, unlike for the pure powder, the presence of LTO and CB results in an increase in the decomposition temperature of the PVDF. This increase is indicative of the interaction between the PVDF and the LTO particles, as evidenced by the FT-IR spectra of the PVDF and the DS-LTO electrodes (Fig. S6).

The difference in the electrochemical performance was further characterized via electrochemical impedance spectroscopy (EIS) measurements performed using half-cells consisting of DS-LTO electrodes that had undergone one cycle. These spectra (Fig. 5a) were interpreted on the basis of the simple equivalent circuit model (shown in the inset in Fig. 5a). For example, an intercept of the  $Z_{re}$  axis at high frequency is associated with the ohmic resistance ( $R_b$ ), i.e., the bulk resistance of the electrolyte and electrical contacts;  $R_{ct}$  and  $Z_w$  represent the charge-transfer resistance at the electrolyte/electrode interface and the Warburg impedance, respectively. Moreover, the constant phase element (CPE) is used instead of a pure capacitive element ( $C_{dl}$ ) in order to account for the roughness of the particle surface [33,34]. The parameters of each electrode, as obtained from the equivalent circuit, are listed in Table 1. The corresponding Nyquist plots are all described by a compressed semicircle combined with a straight line, indicating that the electrode reactions are governed by charge-transfer and diffusion processes. In addition,  $R_b$  and  $R_{ct}$  of the DS-LTO-60 electrode are smaller than those of the other electrodes; these smaller resistances stem from the electrical connection between the particles (and/or particle and the substrate) (Fig. 3) and the increased kinetics of the electrode reaction, respectively. The improved kinetics results from an increase in the number of conductive pathways through the particle network; i.e., the high interparticle connectivity per unit electrode volume of the DS-LTO-60 electrode leads to a reduction in the  $R_{ct}$ . This is also confirmed by calculating the lithium-ion diffusion coefficient, since  $R_{ct}$  is governed by the conductivity of  $Li^+$  ions and electrons. The  $Li^+$ -ion diffusion coefficient ( $D_{Li^+}$ ) of the DS-LTO electrodes, which reflects the charge transfer kinetics, is calculated from [35,36].

$$D = R^2 T^2 / 2A^2 n^4 F^4 C^2 \sigma^2 \quad (1)$$

$$Z_{re} = R_b + R_{ct} + \sigma \omega^{-1/2} \quad (2)$$

where  $R$ ,  $T$ ,  $A$ ,  $n$ ,  $F$ , and  $C$  are the gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), absolute temperature, surface area of the electrode, number of electrons involved in the half-reaction (equal to 1), Faraday constant ( $96,485 \text{ C}\cdot\text{mol}^{-1}$ ), and the molar concentration of  $\text{Li}^+$  ( $4.37 \cdot 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$ ), respectively. The Warburg impedance coefficient ( $\sigma$ ), which is related to  $Z_{re}$  through Equation 2, is obtained from the slope of  $Z_{re}$  and  $\omega^{-1/2}$  ( $\omega$ : angular frequency) in Fig. 5b. Furthermore, the values of the exchange current density ( $i_0$ ) listed in Table 1 were calculated from the following equation [37,38].

$$i_0 = RT / nFAR_{ct} \quad (3)$$

As the table shows,  $i_0$  and  $D_{\text{Li}^+}$  of the DS-LTO-60 were larger than those of the other DS-LTO electrodes. This suggests that, compared to the other electrodes, the DS-LTO-60 has a better electrical conductivity, which facilitates both electron and  $\text{Li}^+$  transport in the electrode. Therefore, the interparticle connectivity of the 60-min-hot-pressed DS-LTO electrode results in reduced resistance owing to increases in the electronic conductivity and the  $\text{Li}^+$  diffusion coefficient. These, in turn, affect the  $\text{Li}^+$  storage capacity, as confirmed by the charge/discharge profiles in Fig. 2.

The DS-LTO-60 electrode exhibited excellent electrochemical properties, and was therefore investigated in further detail for use in high-power LIB applications. Figure 6a shows the initial charge/discharge curves of the DS-LTO-60 at different current rates and a voltage range of 1.0-2.5 V (vs.  $\text{Li}/\text{Li}^+$ ). The electrode exhibits a first charge capacity of  $162 \text{ mAh}\cdot\text{g}^{-1}$  at 0.2 C, and the initial charge capacity at 2 C decreases to  $90 \text{ mAh}\cdot\text{g}^{-1}$ . As expected,

the capacities of the electrodes decreased with increasing current rates. Figure 6b shows the cycling performance of the DS-LTO-60 electrode at a current density of 1 C ( $175 \text{ mA}\cdot\text{g}^{-1}$ ). As the figure shows, the specific capacity decreases from  $120 \text{ mAh}\cdot\text{g}^{-1}$  at the first cycle to  $83 \text{ mAh}\cdot\text{g}^{-1}$  at the 100<sup>th</sup> cycle. This reduction corresponds to capacity retention of 69.4% and stems from the non-porous microsphere LTO employed in this work (Fig. S3). Nano-sized materials having high surface area lead to more effective electrochemical reactions than those occurring in their micro-sized bulk counterparts [39,40]. Therefore, high-surface-area nanomaterials increase the electrolyte/electrode interface and enhance the  $\text{Li}^+$  diffusion rate, which result in increased charge/discharge rates. The electrochemical performance of the electrodes fabricated in this work is superior to that of the conventional micro-sized LTO obtained via slurry casting. Moreover, the performance of the DS- LTO electrode prepared by the dry-spraying method is comparable to those reported in the literature (Table S1). Applying the porous nano-sized LTO or LTO coated with conductance material in the dry-spraying process, should therefore result in significantly improved rate capabilities. As such, we believe that the dry-spraying method used in the present work is especially well suited for commercial-scale mass production of reproducible electrodes.

To optimize the performance of the electrode, the effect of pressure and composition will be investigated further by conducting detailed electrochemical tests, mechanical/physicochemical property measurements, and so on. Other binder polymers and/or active materials are also currently being evaluated. The results obtained from these studies will be published in a separate paper.

#### **4. Conclusions**

We fabricated an LTO electrode using the dry-spraying method as a facile solvent-free direct coating process. In this process, an electrode component mixture, in powder form, was

sprayed on a substrate to form a homogeneous electrode and then isothermally hot-pressed for various times; a schematic of the entire electrode formation process was provided. When the electrochemical performance was measured, the dry-sprayed LTO electrode obtained at a hot-pressing time of 60 min was found to have the most suitable electrode structure; i.e., this electrode consisted of many interconnected particles per unit electrode volume that facilitated electron and lithium-ion transport via shortened pathways within the electrodes. This, in turn, resulted in higher electrical activity and  $\text{Li}^+$  storage capacity compared to those of the other DS-LTO electrodes. We believe that the dry-spraying method has significant potential as an electrode manufacturing process for electric vehicles requiring inexpensive, time-saving, and eco-friendly large-scale LIBs.

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### **Appendix A. Supplementary data**

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2015.xx.xxx>.

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## Table Captions

Table 1. Parameters of DS-LTO electrodes obtained from EIS

Electrode	$R_s$ [ohm]	$R_{ct}$ [ohm]	D [cm <sup>2</sup> ·s <sup>-1</sup> ]	$i_0$ [mA·cm <sup>-2</sup> ]
DS-LTO-30	15.40	142.6	$1.92 \cdot 10^{-12}$	0.23
DS-LTO-45	3.53	88.4	$1.04 \cdot 10^{-11}$	0.37
DS-LTO-60	2.50	63.5	$1.15 \cdot 10^{-11}$	0.52
DS-LTO-90	10.49	94.7	$9.96 \cdot 10^{-12}$	0.35

## Figure Captions

Figure 1. A schematic of the entire manufacturing process of the DS-LTO electrode.

Figure 2. Initial charge-discharge curves of the DS-LTO electrodes, obtained at different HP times, for testing at a rate of 0.2 C and voltages of 1.0-2.5 V (vs. Li/Li<sup>+</sup>).

Figure 3. Illustration of the morphologies of DS-LTO electrodes obtained at different HP times: (a) 30 min, (b) 45 min, (c) 60 min, and (d) 90 min.

Figure 4. TG/DSC curves of the DS-LTO electrodes obtained at different HP times.

Figure 5. Electrical performance of DS-LTO electrodes obtained at different HP times showing (a) typical Nyquist plots. Inset shows the equivalent circuit model, and (b) real parts of the complex impedance versus  $\omega^{-1/2}$ .

Figure 6. Electrical performance of the DS-LTO-60 electrode showing the (a) rate capability at different C-rates and (b) cycle performance at a rate of 1 C.