



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



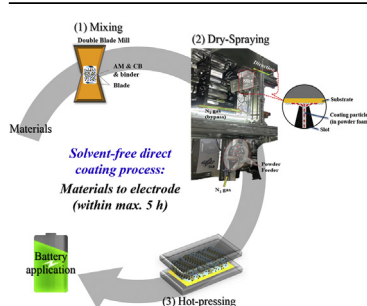
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## HIGHLIGHTS

- We demonstrate a rapid and facile novel solvent-free direct coating process.
- The hot-pressing time had an effect on the electrode morphologies and performance.
- The DS-LTO-60 electrode showed excellent electrical conductivity and  $\text{Li}^+$  storage.
- Dry-spraying process has significant potential as an important industrial technique.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 16 July 2015  
Received in revised form 27 November 2015  
Accepted 17 December 2015  
Available online 30 December 2015

### Keywords:

Dry-spray coating  
Solvent-free  
Battery  
LTO

## 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.

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## 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

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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 (MOx), 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, MOx, 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 (Fig. S1). However, the as-dry-sprayed LTO electrode was isothermally hot-pressed at 175 °C, under a pressure 6 kg  $\text{cm}^{-2}$ , 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 449C). 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.

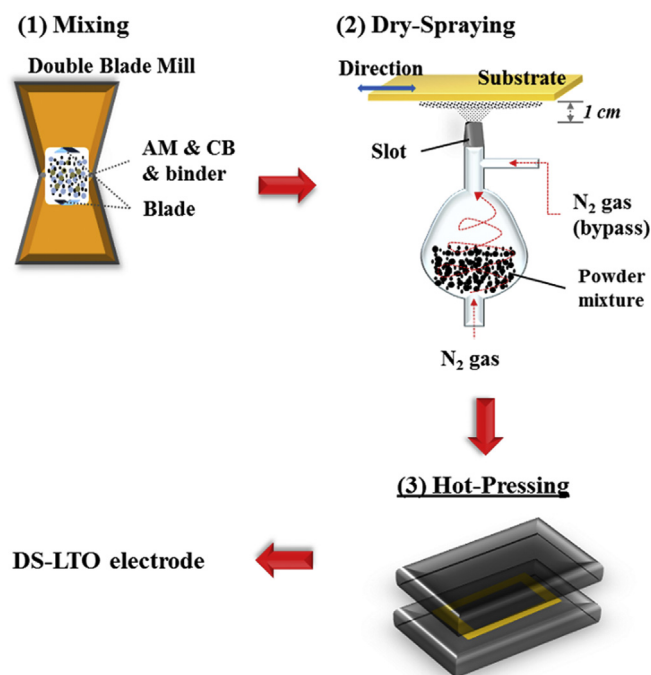


Fig. 1. A schematic of the entire manufacturing process of the DS-LTO electrode.

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