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Fabrication and performance of $Li_4Ti_5O_{12}$/C Li-ion battery electrodes using combined double flame spray pyrolysis and pressure-based lamination technique

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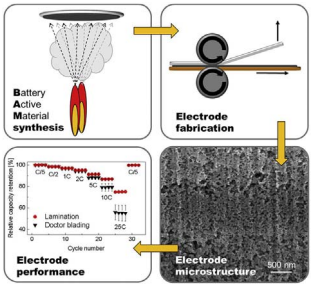
HIGHLIGHTS

- Solvent-free and binder-free Li-ion battery electrode preparation.
- Double flame pyrolysis for pure phase LTO/C nanocomposite.
- Fully-functional battery electrode by single step lamination.
- Long-term cycling and rate capabilities are superior to blade casted electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

Reduction of lithium-ion battery (LIB) production costs is inevitable to make the use of LIB technology more viable for applications such as electric vehicles or stationary storage. To meet the requirements in today's LIB cost efficiency, our current research focuses on an alternative electrode fabrication method, characterized by a combination of double flame spray pyrolysis and lamination technique (DFSP/lamination). *In-situ* carbon coated nano-$Li_4Ti_5O_{12}$ (LTO/C) was synthesized using versatile DFSP. The as-prepared composite powder was then directly laminated onto a conductive substrate avoiding the use of any solvent or binder for electrode preparation. The influence of lamination pressures on the microstructure and electrochemical performance of the electrodes was also investigated. Enhancements in intrinsic electrical conductivity were found for higher lamination pressures. Capacity retention of highest pressurized DFSP/lamination-prepared electrode was 87.4% after 200 dis-/charge cycles at 1C (*vs.* Li). In addition, LTO/C material prepared from the double flame spray pyrolysis was also used for fabricating electrodes *via* doctor blading technique. Laminated electrodes obtained higher specific discharge capacities compared to calendered and non-calendered blade-casted electrodes due to superior microstructural properties. Such a fast and industrially compelling integrative DFSP/lamination tool could be a prosperous, next generation technology for low-cost LIB electrode fabrication.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) are known for their high energy/power density, high efficiency and long cycle life, making this battery type to the power source of choice for the electronic consumer market [1,2]. A major drawback for the success of LIBs determined for electromobility and large-scale energy storage devices is the high production cost per kWh [3,4]. Innovations and optimizations in production, process and automation engineering of large-scale LIB production lines are of particular importance to enhance the cost efficiency [5–7]. In 2015, "Production Engineering of *e*-Mobility Components" (PEM) of RWTH Aachen forecasted the approximate investment need of 372.6–557.4 Mio. € to acquire the facilities necessary for producing 2.2 GWh/year (10^7 cells per year with a total cell capacity of 60 Ah) [8]. The underlying conventional LIB production route consists of three major steps: (1) electrode preparation (2) cell assembly, (3) formation and aging. Among these, the electrode manufacturing is the most complex and labor-intensive process [8–10]. Starting from pristine battery active materials (BAMs), electrode construction spans four steps, complicated slurry production, doctor blading (DB), drying, and calendering [8].

Economic progress was already achieved by fine-tuning this slurry-based electrode manufacturing procedure [11–13]. Obviously, another very effective factor to reduce production costs is to further diminish or completely avoid the amount of certain electrochemically inactive components used for battery cell construction. More specifically, a minimization/avoidance of involved additives such as solvents (for slurry preparation) and electrochemically inactive organic binders, would be a great leap forward in terms of cost efficiency [14,15].

Depending on the field of application, there are numerous BAMs available that are used by the battery manufacturers. A combination of common lithium transition metal oxide cathodes with spinel lithium titanate ($Li_4Ti_5O_{12}$, LTO) based anodes could result in battery cells with very high cycle life capabilities. LTO is well-known for its low-reactivity with common inorganic electrolytes, negligible volume changes and a stable voltage plateau of 1.55 V (*vs.* Li/Li^+) [16–20]. The major drawbacks of LTO are its intrinsically low ionic diffusion coefficient (10^{-9} to 10^{-16} cm^2/s) and poor electrical conductivity (10^{-13} S/cm), preventing the material from reaching its predicted maximum theoretical capacity of 175 mAh/g during high dis-/charge rates [21]. Two typical approaches have been developed over the past few years to overcome these drawbacks [22]. First, the poor ionic conductivity can be enhanced by downsizing the LTO particle sizes to the nano-regime. Thereby, the inner-particle lithium-ion diffusion pathway during de-/intercalation is reduced and the reactive contact area between the electrolyte and the LTO active material is increased [23,24]. Secondly, the electrical conductivity can be significantly increased by surface modifications [22]. Especially carbon coatings serve as multifaceted layers between electrode and electrolyte due to their excellent electrical conductivity and superior electrochemical stability [22,25].

Prominent approaches for decreasing particle size and carbon functionalization of LTO particles comprise solid state, sol-gel, and hydrothermal syntheses [26–28] which are, among other methods, comprehensively summarized by Yi et al. and Sun et al. [18,21]. Although enabling the production of high rate capable LTO active material with long cycle life, those techniques often suffer from very complex multistep processing protocols and require long time and high energy consumption. Likewise, the nature of carbon species and its distribution cannot be easily controlled.

In recent years, the flame spray pyrolysis (FSP) technique has emerged as a powerful tool for BAM synthesis, enabling the design of high-purity, crystalline and uniform oxide nanoparticles (NPs) with a narrow particle size distribution [29–37]. The process is highly scalable and reproducible, making FSP a versatile technique for large scale NP production [32–40]. FSP has already been successfully applied to the synthesis of crystalline nano-sized LTO particles, resulting in enhanced high power capability ascribed to the increased Li-ion diffusion coefficient [19,23,24,41–43]. Combining two FSP reactors (double flame spray pyrolysis, DFSP), material design becomes more flexible since composite materials with finely tuned properties (compositions, size) can be achieved *via* individual control over the respective flame spray parameters [36,44–54].

In the current proof-of-principle, an unprecedented approach for the fabrication of cost-efficient and well-performing LTO-based electrodes is established using a single-step, dry, *i.e.* solvent-free, and binder-free technique. To the best of our knowledge, DFSP is applied for the very first time to *in-situ* carbon functionalize LTO particles (LTO/C), followed by electrode assembly using a pressure-based lamination technique [55,56].

The resulting material's phase composition, particle sizes, morphology, carbon content and structure were thoroughly characterized using X-ray powder diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and Raman spectroscopy. From the synthesized LTO/C particles, electrodes were fabricated using two pressurized rollers for direct lamination of LTO/C on the copper current collector. Calendered and non-calendered LTO/C electrodes were assembled from the same LTO/C composite material, using a conventional slurry-based DB technique. To extract the electrochemical performance, electrodes fabricated by pressure-based lamination and DB technique were characterized in LIB half-cells *via* galvanostatic dis-/charge measurements.

2. Experimental

2.1. Nanoparticle synthesis using DFSP

Ultrafine LTO/C was synthesized with FSP using two individual flame spray reactors. One individual flame was used for spraying a precursor solution to obtain LTO and the second flame for spraying xylene (> 97%, VWR Chemicals) as the carbon precursor. The two-flame (two-solutions) setup was preferred over a one-flame setup to achieve a higher control of the oxygen content in the two disparate oxygen-sensitive systems, *i.e.* LTO (formation requires oxygen) and carbon (oxygen must be low/absent to obtain elemental carbon). The precursor solution for LTO was prepared by dissolving lithium acetylacetonate (Li (acac), 97%, Sigma-Aldrich) and titanium *tert*-isopropoxide (TTIP, 97%, Sigma-Aldrich) separately in an equal volume fraction of toluene (99%, VWR Chemicals) and 2-ethyl hexanoic acid (EHN acid, ≥99%, Sigma-Aldrich) with a total metal concentration of 0.5 M [42]. The lithium and titanium containing solutions were mixed in the stoichiometric ratio of Li/Ti = 4/5. The LTO precursor solution and xylene were individually delivered using syringe pumps (KDS-100-CE, KDS Scientific) into the independent FSP nozzles at a rate of 5 mL/min each, maintaining the pressure drop of ~1.5 bar at both nozzle tips. The LTO precursor solution was atomized with oxygen (5 L/min, nozzle pressure drop 1.5 bar) and combusted using premixed methane (1.5 L/min) and oxygen (3.2 L/min) gas (burning), resulting in the LTO spray flame (Fig. 1, step 1). Operating principle of the FSP reactor is thoroughly described by several authors [32,33,36,50].

In general, particles are formed *via* droplet-to-particle conversion at low temperatures and gas-to-particle conversion at higher temperatures. In flame aerosol process, gas-to-particle conversion results into ultrafine single crystalline nanoparticles. Selection of highly combustible organic solvents and precursors are crucial to obtain such particles during combustion. The requirement for the flame aerosol process is that the precursor solvents are (1) stable at room temperature (2) volatile at elevated temperatures and (3) reactive with oxygen in the gas phase, while these requirements are interdependent [43]. Within the flame spray, the nanostructured LTO particles are formed at temperatures of ≥2000 °C upon nucleation, surface growth, coagulation and coalescence [37]. To synthesize carbon from xylene, it is important to prevent carbon particles from oxidation. Accordingly, nitrogen gas was