Solvent-Free Dry Powder Coating Process for Low-Cost Manufacturing of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Cathodes in Lithium-Ion Batteries

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Abstract

We report a solvent-free dry powder coating process for making $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) positive electrodes in lithium-ion batteries. This process eliminates volatile organic compound emission and reduces thermal curing time from hours to minutes. A mixture of NMC, carbon black, and poly(vinylidene difluoride) was electrostatically sprayed onto an aluminum current collector, forming a uniformly distributed electrode with controllable thickness and porosity. Charge/discharge cycling of the dry-powder-coated electrodes in lithium-ion half cells yielded a discharge specific capacity of 155 mAh g^{-1} and capacity retention of 80% for more than 300 cycles when the electrodes were tested between 3.0 and 4.3 V at a rate of C/5. The long-term cycling performance and durability of dry-powder coated electrodes are similar to those made by the conventional wet slurry-based method. This solvent-free dry powder coating process is a potentially lower-cost, higher-throughput, and more environmentally friendly manufacturing process compared with the conventional wet slurry-based electrode manufacturing method.

Keywords: Solvent-free; Lithium-Ion battery; Cathode materials; NMC; Dry-powder-coated

1. Introduction

Lithium-ion batteries (LIBs) dominate the market of energy-storage systems utilized in portable consumer electronic devices due to their high operating voltage, good rate capability, and long cycle lifetime[1-6]. While LIBs are popularly used in portable devices, state-of-the-art

LIBs are behind the target needed for widespread adoption in vehicular applications and large-scale stationary storage systems. The Department of Energy suggests that energy-storage systems must meet a cost target of \$125 kWh⁻¹ to meet the requirements for widespread adoption, which would require a three- to four-fold reduction in system costs[7]. In a recent publication, Wood and coworkers suggest (1) reducing electrode processing costs associated with organic solvents and their drying time and (2) increasing electrode thickness without compromising power density as two ways to significantly reduce system costs in LIBs [8].

The most commonly employed wet slurry-based coating method for electrode fabrication involves the mixing of active material, polymer binder, and conductive additive in a solvent. The slurry is then coated onto current collectors, dried, and calendared. *N*-methylpyrrolidone (NMP) is the most commonly used organic solvent to dissolve the poly(vinylidene difluoride) (PVDF) binder in electrode fabrication. Evaporation of NMP requires a significant energy investment, as electrodes must be dried for several hours at temperatures as high as 120 °C to remove this solvent[9]. Because of NMP's high cost and potential as an environmental pollutant, solvent recovery is necessary in commercial applications, adding further costs to battery fabrication [8]. Numerous research groups have explored the possibility of removing organic solvents from electrode fabrication to reduce costs and environmental impact.

By replacing traditionally utilized PVDF with polymer binders such as carboxymethyl cellulose (CMC) [10, 11], alginate [12], and fluorine acrylic latex (TRD 202A) [13], water can be used instead of NMP as the solvent for electrode preparation. In several publications, water-based slurries have been reported to create electrodes with comparable performance to those fabricated with NMP [13]. Using water as the solvent eliminates the use of organic solvents, however, the time-intensive and energy-demanding drying step can be further optimized to

reduce the cost of battery fabrication. For these reasons, new methods of electrode fabrication have been explored to eliminate the use of solvents altogether.

Solvent-free coating process utilizing dry particles is an ideal alternative solution to replace the wet slurry-based manufacturing process, as it eliminates the cost of solvents as well as the cost of their removal and recovery. Solvent-free manufacturing has been achieved through pulsed-laser deposition, a method in which a laser is focused on to-be-deposited electrode components. This technique requires high vacuum (10^{-6} Torr) and high annealing temperatures (>600 °C), producing only thin films of cathode material (<500 nm) [14, 15] and is therefore impractical for large-scale fabrication. While Radio frequency (RF) magnetron sputtering can be used with lower temperature substrates (350 °C), it requires expensive instrumentation and inert atmospheres, again impractical for large-scale electrode fabrication [16].

Another method for dry-powder coating is Electrostatic Spray Deposition (ESD), a solvent free technology that has been used in coating industries for over 30 years to create decorative and functional paints and coatings. This method eliminates the release of volatile organic compounds (VOCs), reduces energy consumption, increases paint material transfer efficiency, and improves painted-surface quality. In ESD, particles are charged as they pass through a charging gun, and are deposited onto a grounded surface [17]. This method can be used on large particles and is scalable, offering high deposition rates onto large surfaces [18].

Recently Hiroya *et al.* reported the fabrication of cathodes using a tribo-charging gun that made of a polytetrafluoroethylene (PTFE) gun, which produces mostly positively charged particles. The cathodes coated on aluminum current collectors at room temperature contained LiCoO_2 particles (LCO, ~ 2 μm in diameter) as the active material, carbon black particles (~ 40 nm) as the conductive agent, and poly(methyl methacrylate) particles (~ 100 nm) as the binder.

These subsequently roll-pressed electrodes (ca. 70 μm thick) were reported to have a capacity of ca. 140 mAh g^{-1} in lithium half cells charged at 0.1C for one cycle [19]. More recently Ludwig *et al.* reported the use of ESD, followed with hot-rolling treatment, to create 40-130 μm thick cathodes containing a 90:5:5 ratio of LCO:carbon additive:PVDF with ca. 30% porosity, which delivered specific capacity of 121 mAhg^{-1} at a charge rate of 0.1 C in lithium half cells [20]. Similarly prepared cathodes containing $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) as the active material were also reported, showing 138 mAhg^{-1} in lithium half cells [20].

In this study, we sought to (1) further demonstrate laboratory scale solvent-free dry powder coating processes for making LIB cathodes, and (2) compare in detail the performance and durability of electrodes made by dry powder coating processes with that by wet slurry coating processes and to other cathodes prepared by this method.

2. Experimental

2.1 Electrode Fabrication

2.1.1 Dry-Powder-Coated Electrodes. To prepare the dry cathode mixture, NMC (Umicore) was mixed with carbon black (CB, Super P C65, TIMCAL) in a planetary mixer-deaerator (Mazerustar KK-50S, Kurabo) for 20 min. The NMC particle size is between 5.6 μm and 12 μm ($D_{50}=10.0$). The resultant mixture was combined with PVDF (kf 1100, Kureha America) to create a mixture of NMC:CB:PVDF with a weight ratio of 19:1:1, which was obtained after mixing in a ball mill (8000M Mixer/Mill, SPEX) for 30 min.

The electrostatic dry-powder-coating process for electrode fabrication utilized a corona-type electrostatic spray gun setup (Figure 1) inside a spray booth to capture loose powder, which was used to spray the powder mixture onto an electrically grounded Al foil (15 μm thick). The DC voltage between the gun and Al foil was set at 25 kV. Compressed air (15 psi) was used

to transport the powder mixture from the hopper to the spray gun. The distance between the tip of the spray gun and the substrate was fixed at 20 cm. The angle between the spray direction and the normal of the Al foil was 45°. The thickness of the sprayed layer was controlled by keeping the spraying time to 1 min, and the size of the fabricated electrode layer was about 18 mm wide and 25 mm long. The dry-powder-coated electrodes were transferred to an oven and heated in air for 1 h at 170 °C. Then the baked electrodes were calendered at room temperature with specified gap spacing by a compact electrical rolling press (MTI Corp.). 12 mm diameter discs were cut using a Precision Disc Cutter (MTI Corp.) and transferred to a glove box.

2.1.2 Wet-Slurry-Coated Electrodes. For comparison, slurry-based electrodes were prepared from NMC, CB, and PVDF (19:1:1 wt. ratio) suspended in NMP (84% in volume, BASF). The slurry was blended in a homogenizer at 4000 rpm for 1 h (Polytron PT 10-35 GT) and afterward was casted onto Al foil (15 µm thick) using a compact-tape casting coater with integrated dryer and vacuum chuck (MTI Corp.). The adjustable doctor blade gap was set to 200 µm, and slurry was cast at a speed of 0.2 m min⁻¹. The electrodes were dried in air overnight and calendered in a compact electric rolling press (MTI Corp.) with adjusted clamping force at room temperature. After calendering, 12 mm diameter discs were cut using a Precision Disc Cutter (MTI Corp.) after which they were placed in a vacuum oven at 130 °C for 12 h.

2.2 Electrode Characterization

2.2.1 Morphology. Using an Environmental Scanning Electron Microscopy (ESEM) with Energy Dispersive Spectroscopy (EDS) (Quanta FEG 250, FEI), we investigated the morphology and composition of the powders, as well as the surface and cross section of the electrodes made by the electrostatic spray and wet slurry coating processes.

2.2.2 Thermogravimetric Analysis. Thermogravimetric Analysis (TGA) was used to determine the mass ratios of the powder mixtures consisting of NMC, CB, and PVDF before and after electrostatic spraying. TGA experiments were performed on TA Q500 instrument, with a standard heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from ambient temperature to $800\text{ }^{\circ}\text{C}$ under air.

2.2.3 Coin Cells Assembling and Electrochemical Tests. CR2025-type coin cells were assembled using an automatic coin cell crimper (KTE-20S-D, Hohsen) inside argon filled glovebox (MB-20-G, MBraun) with water and oxygen levels below 0.1 ppm. Lithium metal foil (99.9%, Sigma–Aldrich) was used as the counter/reference electrode. A piece of poly-propylene membrane (Celgard 2400) was used as the separator between the lithium foil and the cathode. 1M LiPF_6 in ethylene carbonate/ethylmethyl carbonate (EC/EMC 3:7 by volume, BASF) with 2% vinylene carbonate (VC, BASF) was used as the electrolyte. The electrolyte weight ratios were 12.5 wt% LiPF_6 , 25.7 wt% EC, 59.9 wt% EMC, and 2.0 wt% VC. A stainless steel spacer and spring were placed on the lithium metal to obtain a uniform current distribution and served as a current collector. The electrochemical characterization of the assembled cells was performed using a multi-channel potentiostat (VMP-3, Bio-logic) operated in the galvanostatic mode. Cell cycling was performed at room temperature with a 2 h resting period before each test. Charge/discharge tests were also performed at variable rates, ranging from 0.5C to 10C, cycling between 3.0 V and 4.3 V. At the end of each charge, the electrode was holding at 4.3 V until the current dropped below 0.05C. More than 20 coin cells from 3 batches were made to test the electrochemical performance of the prepared electrodes by the dry-process and wet-process methods in half-cells with pure lithium as the counter electrode.

Figure 1. Illustration of an electrostatic dry-powder coating process for making cathodes containing NMC, carbon black, and PVDF.

3. Results and discussion

NMC was used as the cathode active material because of its high reversible specific capacity ($150\text{--}200\text{ mAh g}^{-1}$) [21], high energy density ($140\text{--}180\text{ Wh/kg}$) [22], and high charge and discharge rate capability [23]. The dry-powder-coated electrodes were transferred to an oven set at $170\text{ }^{\circ}\text{C}$, close to the melting point of PVDF ($177\text{ }^{\circ}\text{C}$) and were heated in air for 1 h. The heating temperature was close to melting point of PVDF to build bonding between PVDF and the solid particles (NMC and CB), meanwhile maintain the porosity of electrodes during heating[24]. The baked electrodes were calendered at room temperature to increase the cohesion between the particles and the binder hence improve the integrity of the electrodes. The calendering process could also improve the adhesion between the coated materials and the Al foil, and control the porosity and the packing density of the electrodes.

To determine whether the dry-powder-coated electrodes contained the target ratio of NMC:CB:PVDF with as-prepared mixture of powders, we analyzed the pre-mixed powder and that deposited on the Al foil using TGA. For the powder mixture and coated electrodes, mass loss trends (Figure S1a in the supplementary information) were nearly identical. Comparing the TGA plots of the mixtures to that of the components shown in Figure S1b, it is evident that the mass loss spanning ca. 400 to 460 °C corresponds to PVDF[25, 26], whereas the loss from 500 to 600 °C corresponds to CB. In the temperature window analyzed, NMC does not lose mass, which means it is thermally stable[27].

SEM was used to analyze the powder mixtures to determine whether the particles remained intact after electrostatic coating. SEM images (Figure 2a-b) indicate that the NMC particles are intact after processing, as no appreciable morphological difference is observed before and after coating. The SEM image of the top surface of the as-prepared electrode after the curing and calendaring steps (Figure 2c) shows that the electrode is more dense after processing. Figure S2 in the supplementary information shows the even distribution of the electrode particles over a large electrode area. For comparison, a top view of a slurry-made electrode after drying and calendaring is shown in Figure 2d.

Figure 2. Top-view SEM images of: (a) Powder mixture before dry-powdercoating. (b) Powder mixture after dry-powdercoating. (c) Dry-powder-coated electrode after calendering. (d) Wet-slurrycoated electrode after drying and calendering.

Cross-sectional SEM images of the dry-powder-coated electrodes after calendering are shown at two magnifications in Figures 3a-b. For comparison, the SEM cross-section image of an electrode made by the traditional wet-slurry method is shown in Figure 3c. The structures of the electrodes made by the two processes are similar. EDS was used to map the elements carbon, oxygen, and fluorine (Figures 3d-f). Based on the oxygen and fluorine maps, respectively, the EDS maps show that NMC and PVDF are dispersed throughout the sample. Although the carbon map shows the presence of carbon throughout the image, because carbon is present in both carbon black and PVDF, it is not possible to differentiate between these species.

Figure 3. SEM images of the cross-section of the dry-powder-coated electrode after calendaring (a) and magnified cross-sectional view (b). A cross-sectional view of the wet-slurry-coated electrode (c). EDS maps of the elements carbon (d), oxygen (e), fluorine (f) from image (b).

The calendaring process compacts the electrodes, improves the cohesion between the particles and the adhesion of the composite materials with the Al foil, and controls the porosity and the packing density of the electrodes[28, 29]. The electrodes are well compacted after calendaring with a porosity of 31% and packing density of 2.5 g cm^{-3} . For comparison, two conventional slurry-based electrodes with mass loading higher and lower than the dry-powder coated electrode were studied.

Table 1. The thickness, mass loading, porosity, density, and discharge capacity of electrodes made by the dry and wet processes.

Process	Thickness (μm)	Mass loading (mg cm^{-2})	Porosity (%)	Packing density (g cm^{-3})	Discharge capacity (mAh g^{-1})
Dry-powder coating electrode	40.5	10.07	31	2.5	155
Wet-slurry-based electrode (higher loading)	52	14.27	35	2.7	156
Wet-slurry-based electrode (lower loading)	32.6	7.65	41	2.4	157

The electrochemical behavior of dry-powder-coated electrodes was analyzed in lithium half cells using 1M LiPF_6 in EC/EMC (3:7 by volume) containing 2 wt% VC as the electrolyte. VC was added to improve the rate performance [30]. Cell potential vs. state-of-charge plot for the first cycle of the dry-powder-coated electrode is shown in Figure 4a. For comparison, the first cycle electrochemical behavior of a wet-slurry made electrode is shown in Figure 4b. Evidently, the voltage profiles for charge-discharge cycles for the dry powder-coated electrodes are similar to that of the conventional slurry-coated electrodes.

Figure 4. Cell potential vs. Capacity for the first charge and discharge cycles of the dry-powder-coated electrode (a) and wet-slurry-coated electrode (b).

Figure 5a shows the potential profile for cycles 1, 10 and 20 between 3.0 V and 4.3 V at 0.2C with a constant voltage holding with the current limitation of 0.05C at the end of the charge step. For dry-powder coated electrodes, the initial discharge capacities fade slowly during cycling and are 155 mAh g⁻¹ and 153 mAh g⁻¹ for cycles 1 and 20, respectively, while for wet-slurry-coated electrodes there is little capacity fade for the first 20 cycles.

To investigate the effect of different charge/discharge rates on the cycling performance of the dry sprayed and slurry electrodes, the NMC cells were charged and discharged between 3.0 V and 4.3 V at various cycling rates, in the order of 0.2C, 0.5C, 1C, 2C, 5C, 10C and 1C. For dry powder coated electrodes, the specific capacities were 156, 148, 139, 130, 96, 20, and 139 mAh g⁻¹, respectively, as shown in Figure 5b. When returned to 1C, the capacity recovered to the previous level. At high rates, the electrodes will polarize and the plateaus of the NMC become shorter when the charge and discharge current densities increase, causing the decrease of capacity[12]. For the wet-slurry-coated higher mass loading electrode the discharge capacities for the respective C-rates were 153, 149, 145, 140, 129, 46, and 145 mAh g⁻¹, while for the wet-slurry-coated lower mass loading the electrode discharge capacities were 151, 145, 140, 133, 120, 90, and 139 mAh g⁻¹. The small difference in the discharge capacities between the dry-powder and wet-slurry coated electrodes for high charge/discharge rates may come from the differences in porosity and packing density of the electrodes.

Figure 5c shows the long term cycling performance of the dry sprayed and the conventional slurry-made electrode between 3.0 V and 4.3 V at 0.2C followed by constant voltage with current limitation of 0.05C after charge step. For the dry-powder-coated electrode, the first discharge capacity was 155 mAh g⁻¹, and the discharge capacity was 123 mAh g⁻¹ after 300 cycles with a capacity retention of 80%. While for the wet-slurry-coated electrode, the first

discharge capacities were 156 mAh g^{-1} and 157 mAh g^{-1} with capacity retention of 60% and 65% and discharge capacity of 97 mAh g^{-1} and 104 mAh g^{-1} after 300 cycles for higher and lower mass loading respectively. The cycling performance of the dry sprayed NMC electrode is better than that of the traditional slurry-coated electrode by exhibiting stable performance and better capacity retention. These results suggest that (1) the internal resistances are comparable and (2) the NMC is fully utilized in both electrodes.

The post-cycling SEM images, Figs. 6a-6d, were obtained for the electrodes prepared using both methods after 300 cycles. The SEM images show that cracks appeared after cycling in both electrodes. At the end of discharge cycles, the dry-powder electrode images in Figure 6a and b showed that cracks appeared at the NMC grain boundaries, while in the wet-slurry electrode (Figure 6c and d), the crack appeared around the NMC particles and in the CB and PVDF mixture. The size of the cracks in the dry-powder electrode appeared larger than that in the wet-slurry electrode, though the difference in cracking does not seem to be responsible for the slight difference in performance and durability of electrodes made by the two processes.

As reported by Ludwig *et al.* [20], they used electrostatic spray deposition (ESD), followed by hot-rolling treatment, the discharge capacity was 121 mAh g^{-1} in lithium half cells and the capacity retention was 87% at 0.5C after 50 cycles. In this work, we demonstrate that by preheating the electrode film after spray then calendaring it at ambient temperature, the electrode shows an improvement in performance and cycle life.

Figure 5. (a) Potential vs. capacity profiles of the dry-powder-coated cathode in lithium half cells, for cycle 1, 10 and 20. Cells were cycled in the voltage window from 3.0 V to 4.3 V at 0.5C followed by constant voltage holding with current limitation of 0.05C at the end of each charge. (b) Discharge capacities at various current densities for two types of NMC cathodes. (c) Discharge capacity (left) and capacity retention (right) curves for a wet-slurry coated NMC cathode and a dry-powder coated NMC cathode in lithium half cells cycled between 3.0 V and 4.3 V at a rate of 0.5C.

Figure 6. SEM images of the top surfaces of electrodes after 300 cycling at 0.2C over avoltage range from 3.0 V to 4.3 V: (a) the dry-powder electrode, (b) magnified dry-powder electrode view, (c) the low mass loading wet-slurry electrode, and (d) magnified wet-slurry electrode view.

4. Conclusion

We demonstrated that a solvent-free dry powder coating process, in particular electrostatic spraying, can be used to fabricate NMC-containing cathodes for LIBs. The morphology of the powders and electrodes shows very well distributed particles in the coated layer, and that the binder is well dispersed in dry powder before and after spraying. Constant current charge-discharge test results show that the dry sprayed NMC electrodes with PVDF as

binders and CB as a conductive agent exhibit high discharge specific capacity with very good capacity retention, comparable to electrodes made by the conventional, wet-slurry-coating process.

This work is significant because (1) electrodes made by the dry powder coating process can have reversible capacity and cycle life comparable to the electrodes made by the wet slurry method, (2) dry powder coating may lower the cost by reducing the mixing and slurry preparation steps and the reducing drying time, and (3) dry-powder coating eliminates the pollution caused by NMP solvent. Since dry powder coating processes have significantly benefited the paint industry which faced the similar issues with the cost and environmental impact associated with solvents, we believe that solvent-free dry coating processes, such as electrostatic spraying, could replace the traditional wet slurry method of making battery electrodes.

Acknowledgements

We thank Baleegh Sood from Department of Chemical and Materials Engineering and Darius Allen Shariaty from Department of Chemistry, University of Kentucky, for helpful discussions and technical support. Mr. Al-Shroofy expresses his gratitude to the Iraqi Government for the scholarship support.

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Author Contributions

Mohanad Al-Shroofy carried out electrochemical experiment and data analysis and wrote the manuscript. Qinglin Zhang, Jiagang Xu and Tao Chen assisted in experimental work. Aman Preet Kaur carried out TGA measurements.

Notes

The authors declare no competing financial interest.

References

- [1] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R.P. Zaccaria, C. Capiglia, *J Power Sources*, 257 (2014) 421-443.
- [2] N. Nitta, G. Yushin, *Particle & Particle Systems Characterization*, 31 (2014) 317-336.
- [3] M. Obrovac, V. Chevrier, *Chemical reviews*, 114 (2014) 11444-11502.
- [4] L. Zhang, H.B. Wu, X.W.D. Lou, *Advanced Energy Materials*, 4 (2014).
- [5] K. Zhang, Z. Hu, Z. Tao, J. Chen, *Science China Materials*, 57 (2014) 42-58.
- [6] Z. Wang, L. Zhou, *Advanced materials*, 24 (2012) 1903-1911.
- [7] D. Howell, US Department of Energy, Washington, DC, (2012).
- [8] D.L. Wood, J. Li, C. Daniel, *J Power Sources*, 275 (2015) 234-242.
- [9] B. Huang, in, Google Patents, 2013.
- [10] I. Doberdò, N. Löffler, N. Laszczynski, D. Cericola, N. Penazzi, S. Bodoardo, G.-T. Kim, S. Passerini, *J Power Sources*, 248 (2014) 1000-1006.
- [11] N. Loeffler, J. von Zamory, N. Laszczynski, I. Doberdo, G.-T. Kim, S. Passerini, *J Power Sources*, 248 (2014) 915-922.
- [12] J. Xu, S.-L. Chou, Q.-f. Gu, H.-K. Liu, S.-X. Dou, *J Power Sources*, 225 (2013) 172-178.
- [13] Q. Wu, S. Ha, J. Prakash, D.W. Dees, W. Lu, *Electrochimica Acta*, 114 (2013) 1-6.
- [14] S. Shiraki, H. Oki, Y. Takagi, T. Suzuki, A. Kumatani, R. Shimizu, M. Haruta, T. Ohsawa, Y. Sato, Y. Ikuhara, *J Power Sources*, 267 (2014) 881-887.
- [15] N. Kuwata, J. Kawamura, K. Toribami, T. Hattori, N. Sata, *Electrochemistry Communications*, 6 (2004) 417-421.
- [16] K.-F. Chiu, *Thin Solid Films*, 515 (2007) 4614-4618.
- [17] A.G. Bailey, *Journal of electrostatics*, 45 (1998) 85-120.
- [18] M. Mazumder, D. Wankum, R. Sims, J. Mountain, H. Chen, P. Pettit, T. Chaser, *Journal of Electrostatics*, 40 (1997) 369-374.
- [19] H. ABE, A. KONDO, M. NAITO, M. YAMAGUCHI.
- [20] B. Ludwig, Z. Zheng, W. Shou, Y. Wang, H. Pan, *Scientific reports*, 6 (2016).
- [21] D. Mohanty, K. Dahlberg, D.M. King, L.A. David, A.S. Sefat, D.L. Wood, C. Daniel, S. Dhar, V. Mahajan, M. Lee, *Scientific reports*, 6 (2016).
- [22] P. Patel, *ACS central science*, 1 (2015) 161.
- [23] S.-L. Wu, W. Zhang, X. Song, A.K. Shukla, G. Liu, V. Battaglia, V. Srinivasan, *Journal of The Electrochemical Society*, 159 (2012) A438-A444.
- [24] The library of manufacturing, <http://www.thelibraryofmanufacturing.com> (2015).
- [25] L.F. Malmonge, S.d.C. Langiano, J.M.M. Cordeiro, L.H.C. Mattoso, J.A. Malmonge, *Materials Research*, 13 (2010) 465-470.
- [26] J.S.d.C. Campos, A.A. Ribeiro, C.X. Cardoso, *Materials Science and Engineering: B*, 136 (2007) 123-128.
- [27] J. Geder, J.H. Song, S.H. Kang, Y. Denis, *Solid State Ionics*, 268 (2014) 242-246.
- [28] H. Kang, C. Lim, Y. Fu, L. Zhu, (2016).
- [29] Y. Sheng, C.R. Fell, Y.K. Son, B.M. Metz, J. Jiang, B.C. Church, *Frontiers in Energy Research*, 2 (2014) 56.
- [30] R.D. Deshpande, P. Ridgway, Y. Fu, W. Zhang, J. Cai, V. Battaglia, *Journal of The Electrochemical Society*, 162 (2015) A330-A338