

High Energy Li-Ion Electrodes Prepared via a Solventless Melt Process

Ksenia Astafyeva,^[a] Capucine Dousset,^[a] Yannick Bureau,^[a] Sara-Lyne Stalmach,^[a] and Bruno Dufour^{*[a]}

High areal density and high energy Li-ion electrodes were prepared using a high throughput green, solventless and inexpensive melt process leading to electrodes of controlled porosity. Melt formulations were developed for NCA cathodes and graphite anodes. The formulations were based on commercially available and inexpensive elastomeric or thermoplastic binders, conventional conducting fillers and >90 wt% electrode active materials. A large range of loadings could be achieved, from 4 to 40 mg cm⁻² single side. Electrochemical performances in half cells (coin cells) are reported. High capacity and cyclability for high loadings of NCA cathodes and graphite anodes were demonstrated. Areal capacities over 5 mAh.cm⁻² in coin cells were obtained at a C/5 rate. Cycling at high rates, up to 5 C was demonstrated.

Although Li-ion batteries allow the highest autonomy in environmentally responsible electric cars, their manufacturing exhibits significant drawbacks. Conventionally, Li-ion battery electrodes are manufactured by coating N-methyl-pyrrolidone (NMP) based formulations of active cathode or anode materials and a poly(vinyl difluoride) (PVDF) binder, followed by solvent evaporation.^[1,2] The high solid content slurry mixing is difficult and the dispersion requires a continuous mixing upon storage due to the physico-chemical instability of the slurry.^[3] The electrode drying is energy consuming and solvent recycling is mandatory due to the high toxicity and cost of NMP. These drawbacks lead to high manufacturing costs and high scrap rates. Moreover, the use of solvent coating techniques generates cracks in the electrode for high energy electrodes, which require high thicknesses. Reducing costs and increasing energy density and stability are the main barriers for widespread application of Li-ion batteries.^[4] The battery energy density and lifetime depend on the active material stability and voltage but also on the electrode structure and porosity.^[5] The control of the electrode porosity is required to achieve both high power and stability of thick high energy electrodes.^[6]

[a] Dr. K. Astafyeva, C. Dousset, Y. Bureau, S.-L. Stalmach, Dr. B. Dufour

Research and Innovation Center

Hutchinson SA

Hutchinson CRI, Rue Gustave Nourry,

45120 Chalette sur Loing, France

E-mail: bruno.dufour@hutchinson.com

 Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/batt.201900187>

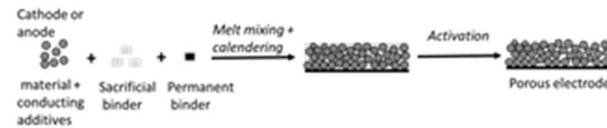
 An invited contribution to a Special Collection dedicated to the Symposium on Batteries and Supercapacitors at the E-MRS Spring Meeting 2019

The use of water as an environmentally friendly method of replacement of NMP has been proposed using water soluble binders.^[7,8] This environmentally friendly approach eliminates the need of solvent recovery. However, getting thick, high energy electrodes with high mechanical integrity remains a challenge due to the use of a dispersion coating technique. Hence, a solvent free approach was proposed.^[9] Other solvent free manufacturing techniques were reported.^[10–13]

Graphite is widely used as an active material for lithium ion anodes.^[14] Several materials are competing as cathode materials, e.g., lithium cobalt oxide (LCO), lithium iron phosphate (LFP), lithium nickel manganese oxide (NMC) or lithium nickel cobalt aluminum oxide (NCA). High energy (up to 300 Wh/kg) and power densities, as well as good life span, make NCA a good candidate for electric vehicles powertrains.^[15]

In this communication, the manufacturing by a solventless melt process and the performances of Li-ion graphitic anodes and NCA cathodes with porosities controlled by the amount of a sacrificial processing aid polymer is described.

Scheme 1 describes the preparation of porous electrodes without any solvent. The electrode melt formulations are detailed in Table 1 and composed of an electrode active material, namely NCA for cathodes or graphite for anodes, conducting additives, a permanent binder and a sacrificial binder. The sacrificial binder, poly(propylene carbonate) (PPC) is used as a processing aid, as well as a porogen additive. In these experiments, the melt mixture was obtained using internal mixers and roll mixers, which are conventional mixers typically used for the formulation of elastomers.^[16] The use of these processes leads to a high shear and high elongational mixing due to the high viscosity of the mixture and an efficient dispersion of the solid materials. The activation step consists in the heat activated quantitative depolymerization of the sacrificial binder into propylene carbonate^[17] and subsequent evaporation of propylene carbonate leading to porous electrodes. The volume of the electrode porosity corresponds to the volume of the sacrificial polymer. The activation step is typically carried out at 250 °C. Depolymerization at temperatures below 100 °C were reported using a catalysis by tertiary amines.^[9] Poly



Scheme 1. Solventless process of porous Li-ion electrodes.

Table 1. Melt formulations and porous NCA and graphite electrode compositions.

	Active material [wt %]	Carbon black [wt %]	Carbon nanofiber [wt %]	Binder [wt %]	PPC liq [wt %]	PPC sol [wt %]
NCA compound	64.0	3.9	1.9	1.3	10.1	18.8
NCA electrode	90	5.5	2.7	1.8	–	–
Graphite compound	61.6	2.7	0.7	2.7	21.0	11.3
Graphite electrode	91	4	1	4	–	–

(propylene carbonate) is a commercial specialty polymer prepared by copolymerization of carbon dioxide and propylene oxide^[18] thus having a positive carbon footprint.^[19]

As shown in Table 1, a mixture of high molecular weight and low molecular weight PPC is used to ensure both a good adhesion to the current collector as well as a good cohesion of the melt formulation under shear. As shown in Table 1, the active material and conducting fillers contents in the melt formulations is very high, above 60 wt%. By comparison, in a conventional solvent based process, the solid content is around 50–60 wt%,^[20] thus leading to a significant shrinkage after solvent evaporation. After activation, active material contents above 90 wt% were obtained, both for the cathode and anode formulations. In the case of NCA formulations, a low content of 1.8 wt% of HNBR as a permanent binder was used in the electrode, which was sufficient to ensure a sufficient electrode cohesion and a good adhesion to the current collector, demonstrated after the removal of the sacrificial polymer using a peeling test. The adhesion score of the cathode was 1 out of 5 according to ISO2409, 0 being best. The score of the graphitic anode on copper was 2. HNBR was already reported as an efficient potential binder.^[21] The thermal treatment applied to remove the sacrificial polymer was found by IR to induce under air a partial crosslinking of the permanent binder.^[22] The thermal treatment on the graphitic anode was carried out under inert atmosphere to avoid the oxidation of copper. No changes were observed on the coated aluminum collectors.

The conducting additives used in the cathode composition were a mixture of carbon black and carbon nanofibers. Carbon nanofibers have been reported as an efficient conducting additive for Li-ion battery electrodes.^[23] Nanofibers also improve the cohesion of the electrode. In the case of the graphitic anode, the binder content was higher, at 4 wt% HNBR due to the low density of graphite. Both for the anode and cathode, the conventional expensive PVDF was replaced by an affordable binder.

Figure 1 shows the rate dependence of the capacity measured at the 5th discharge of a 15 mg.cm⁻² NCA cathode and a 10 mg.cm⁻² graphitic anode prepared without solvents. The porosity of the cathode was 38%, determined using its density. The porosity of the anode was 42%. As shown in Figure 1, the NCA cathodes exhibited a high specific capacity of 160 mAh.g⁻¹ at 0.5 C. The power dependence of the cathode was low up to 2 C. At 5 C, the NCA cathode still had a specific capacity of 40 mAh.g⁻¹. Despite the thermal treatment at 250 °C applied under ambient atmosphere to remove the sacrificial polymer, the electrodes still exhibited a high capacity, even at high power. The power

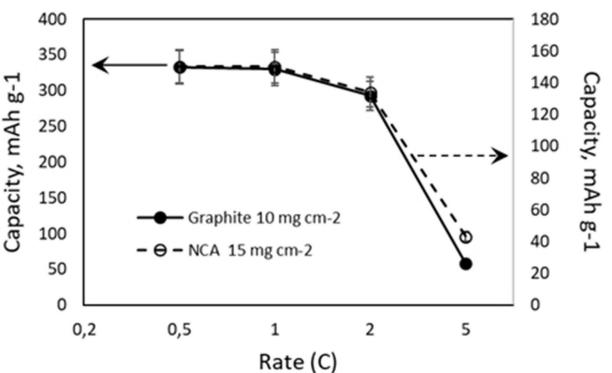


Figure 1. Specific capacity at the 5th discharge of melt processed NCA (shallow dots, right scale) and graphite (full dots, left scale) at different C rates.

dependence is comparable to the reported dependence of conventionally prepared electrodes.^[24–27]

Figure 2 shows the specific capacity of melt processed NCA cathodes at different thicknesses. As shown in Figure 2, NCA cathodes up to 190 µm, which corresponds to a mass loading of 46 mg/cm² still exhibited a high discharge capacity, above 100 mAh/g whereas the capacity dropped at 240 µm, which corresponds to a mass loading of 55 mg cm⁻². The drop in specific capacity at high loading could be due to a high electrode resistance and a lack of conductive pathways along the electrode thickness, as reported elsewhere.^[6] Areal capacities of 5.06 mAh/g at 0.2 C were obtained for a loading of 41.3 mg/cm² for the NCA cathode. For the graphite electrode, an areal capacity of 3.3 mAh/g at 0.2 C were obtained for a loading of 9.3 mg/cm².

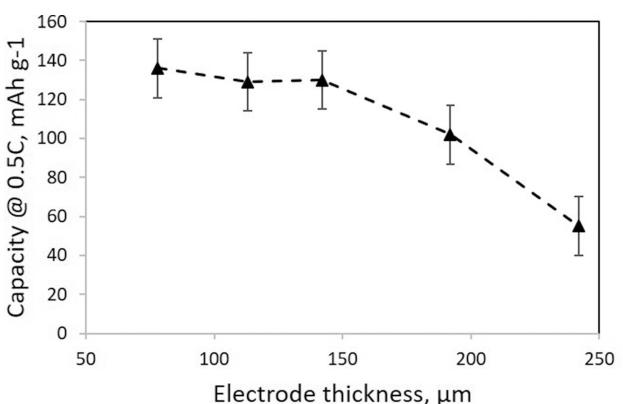


Figure 2. Specific capacity at the 5th discharge of melt processed NCA cathodes at different thicknesses

In summary, a solventless process for lithium-ion cathodes and anodes was reported using melt processes and leading to high capacity electrodes, similar to the capacities of conventional solvent processed electrodes. The process allowed the use of inexpensive elastomer or thermoplastic elastomer binders. The melt processability and the porosity of the electrodes was controlled by the use of a sacrificial binder, namely poly(propylene carbonate), activated by a thermal treatment.

Experimental Section

NCA, SNCA01001 (Targray), natural graphite, SPGPT803 (Targray), Super C65 (Timcal), carbon nanofibers, pyrolyzed cellulose derived (Pyrograph), liquid poly(propylene carbonate) (PPC liq), Converge Polyol 212–10 (Aramco), solid poly(propylene carbonate) (PPC sol), QPAC 40 (Empower Materials), HNBR Zetpol 0020 (Zeon Chemicals), were used as received. The electrodes were prepared as follows: The electrode formulations were mixed via a melt route using a Haake Polylab OS internal mixer with a capacity of 69 cm³ and at a temperature of 70°C. The mixtures thus obtained were calendered at room temperature using a Scamex external roll mixer until a thickness of 200 µm was reached, and they were then calendered again at 50°C to reach the desired thickness. The graphitic anode films were deposited on a copper collector using a sheet calender at 70°C. The NCA cathodes were deposited on a conducting primer coated aluminium collector from Armor. The electrodes obtained were placed in an oven to extract the sacrificial phase. They were subjected to a temperature of 250°C for around 30 minutes, in ambient atmosphere for the NCA cathode and under nitrogen atmosphere for the graphitic anode, until constant weight corresponding to a 100% removal of the sacrificial polymer. The adhesion on the current collector was tested according to standard ISO2409 using a peeling test after crosshatch by a grid of 1 cm² with a 1 mm space. The reference of the applied scotch tape on the crosshatched area was 8402 from 3 M possessing an adhesion strength of 2.6 N cm⁻².

CR1620 coin-type cells (16 mm diameter, 2.01 cm² active surface) consisting of graphite-based or NCA-based working electrode, Celgard 2500 soaked with electrolyte solution, and 75 µm Li foil counter electrode from VWR were assembled inside an Ar-filled glove box (MBraun). The active materials were from Targray, electrolyte solution used was 1 M LiPF6 in 1:1 by weight fluoroethylene carbonate and ethyl methyl carbonate (from Sigma Aldrich). Both H2O and O2 contents were determined to be equal to or less than 0.1 ppm. Galvanostatic testing was performed at different C-rates ranging from C/5 to 5 C, and at a stable temperature of 23°C using a multichannel potentiostat/galvanostat (Bio-Logic VMP3, France). The discharge and charge rates were equal for the cathode and at a charge rate of 0.2 C for the graphite electrode, considering theoretical capacities of 372 mAh/g for graphite and 200 mAh/g for NCA, severally. For each C-rate, the capacity of fifth discharge cycle was considered. The cells were cycled with cut-off voltages of 0.01 V and 1 V for graphite, and 3 and 4.3 V for NCA, respectively.

Acknowledgement

Mélanie Leclerc and Marc Zimmermann are gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Li-ion batteries · dry process · polymers · elastomer

- [1] D. L. Wood, J. D. Quass, J. Li, S. Ahmed, D. Ventola, C. Daniel, *Drying Technol.* **2018**, *36*, 234–244.
- [2] G. Patry, A. Romagny, S. Martinet, D. Froelich, *Energy Sci. Eng.* **2015**, *3*, 71–82.
- [3] W. Bauer, D. Nötzel, *Ceram. Int.* **2014**, *40*, 4591–4598.
- [4] J. Li, Z. Du, R. E. Ruther, S. J. An, L. A. David, K. Hays, M. Wood, N. D. Phillip, Y. Sheng, C. Mao, *JOM* **2017**, *69*, 1484–1496.
- [5] J. Song, J. Kim, T. Kang, D. Kim, *Sci. Rep.* **2017**, *7*, 1–8.
- [6] Z. Du, D. L. Wood, C. Daniel, S. Kalnaus, J. Li, *J. Appl. Electrochem.* **2017**, *47*, 405–415.
- [7] Z. Chen, G.-T. Kim, D. Chao, N. Loeffler, M. Copley, J. Lin, Z. Shen, S. Passerini, *J. Power Sources* **2017**, *372*, 180–187.
- [8] N. Loeffler, G.-T. Kim, S. Passerini, C. Gutierrez, I. Cendoya, I. De Meatza, F. Alessandrini, G. B. Appetecchi, *ChemSusChem* **2017**, *10*, 3581–3587.
- [9] P. Sonntag, D. Aymé-Perrot, B. Dufour, A. Précé, N. Garois, *Process for Preparing an Electrode Composition or Composition with Magnetic Properties, Mixture and Composition Obtained by Means of Said Process and Said Electrode*, **2016**, US20160340476A1.
- [10] B. Ludwig, Z. Zheng, W. Shou, Y. Wang, H. Pan, *Sci. Rep.* **2016**, *6*, 1–10.
- [11] J. Bruckner, S. Tschocke, H. Althues, S. Kaskel, S. Thieme, *Cathode for Lithium-Containing Batteries and Solvent-Free Method for the Production Thereof*, **2015**, US20150061176A1.
- [12] F. Hippauf, B. Schumm, S. Doerfler, H. Althues, S. Fujiki, T. Shiratsuchi, T. Tsujimura, Y. Aihara, S. Kaskel, *Energy Storage Mater.* **2019**, *21*, 390–398.
- [13] X. Xi, S. Raman, *Formulations for and Methods of Fabricating Energy Storage Device Electrodes*, **2018**, US10153096B2.
- [14] S. Passerini, B. Scrosati, *Electrochim. Soc. Interface* **2016**, *25*, 85–87.
- [15] Y. Miao, P. Hynan, A. von Jouanne, A. Yokochi, *Energies* **2019**, *12*, 1074.
- [16] A. K. Bhowmick, H. L. Stephens, *Handbook of Elastomers (Plastics Engineering)*, CRC Press, 2000.
- [17] O. Phillips, J. M. Schwartz, P. A. Kohl, *Polym. Degrad. Stab.* **2016**, *125*, 129–139.
- [18] M. H. Chisholm, D. Navarro-Llobet, Z. Zhou, *Macromolecules* **2002**, *35*, 6494–6504.
- [19] Y. Demirel, *J. Chem. Eng. Process Technol.* **2015**, *0*, 6:3.
- [20] D. Liu, L.-C. Chen, T.-J. Liu, T. Fan, E.-Y. Tsou, C. Tiu, *Adv. Chem. Eng. Sci.* **2014**, *4*, 515–528.
- [21] N. Verdier, S. El Khakani, D. Lepage, A. Précé, D. Aymé-Perrot, M. Dollé, D. Rochefort, *J. Power Sources* **2019**, *440*, 227111.
- [22] N. Verdier, D. Lepage, A. Précé, D. Aymé-Perrot, M. Dollé, D. Rochefort, *J. Polym. Sci. Part A* **2018**, *56*, 1825–1833.
- [23] Y. Yu, Y. Liu, X. Yang, *Alkali-ion Batteries*, IntechOpen **2016**.
- [24] J. Libich, M. Sedláříková, J. Vondrák, J. Máca, P. Čudek, M. Fibek, A. Chekannikov, W. Artner, G. Fafilek, *ECS Trans.* **2018**, *87*, 3–13.
- [25] R. Robert, C. Villevieille, P. Novák, *J. Mater. Chem. A* **2014**, *2*, 8589–8598.
- [26] X. Liu, K. Li, X. Li, *Advances in Green Energy Systems and Smart Grid*, Springer, Singapore, **2018**, pp. 201–213.
- [27] M. A. Hannan, M. M. Hoque, A. Hussain, Y. Yusof, P. J. Ker, *IEEE ACCESS* **2018**, *6*, 19362–19378.

Manuscript received: November 22, 2019

Revised manuscript received: December 11, 2019

Version of record online: January 22, 2020