



Research Article

Novel carbon coating on aluminum current collectors for lithium-ion batteries



Morten Onsrud¹ · Ahmet Oguz Tezel² · Sameer Fotedar^{2,3} · Ann Mari Svensson¹ 

Received: 21 October 2021 / Accepted: 29 June 2022

Published online: 15 July 2022

© The Author(s) 2022, corrected publication 2022 **OPEN**

Abstract

In this work a significant improvement of the performance of LiFePO₄ (LFP) composite cathodes, in particular at high rates (up to 12C), is demonstrated by the use of carbon-coated aluminum current collectors. The coating procedure is novel, and allows for application of a thin carbon layer without the use of solvent and binder. The presence of the thin carbon coating is verified by collecting the Raman spectra. The spectra are dominated by the D-band, indicating a low the degree of graphitization and a high amount of disordered carbon in the sample. LFP cathodes with an area capacity of 1.7 mAh/cm² show an excellent rate capability of 89% upon cycling at 5C. A dramatic reduction of the contact resistance towards the active cathode material has been verified for the coated current collectors. It is furthermore shown that the electrochemical impedance spectra for cathodes applied on uncoated current collectors is dominated by the contact resistance, while the charge transfer resistance dominates the spectrum for cathodes applied to the carbon-coated current collector.

Article Highlights

- A novel carbon coating is applied to aluminum current collectors without the use of solvents and binders
- The rate performance of LiFePO₄ cathodes is considerably improved when the active material is coated onto the carbon-coated collectors
- The contact resistance between the active cathode material and the current collector is almost eliminated by the use of the carbon coating

Keywords LiFePO₄ · Carbon coating · Aluminium current collector · Contact resistance

1 Introduction

LiFePO₄ (LFP) is a well-established, low cost cathode material for Li-ion batteries [1], and a frequently used material for high-power applications. The material has a stable 3D olivine structure, known for its high cycle life. Other advantages include a high theoretical capacity of

168 mA/g, high thermal stability and abundant elements of low toxicity. Lithium intercalation/deintercalation in LFP occurs in a single plateau slightly above 3.4 V, which is also the reason for the somewhat lower energy density of these Li-ion batteries. One drawback of the material is the low ionic and electronic conductivity (< 10⁻⁹ S/cm). For satisfactory performance, the particle size should be small, and

✉ Ann Mari Svensson, annmari.svensson@ntnu.no | ¹Department of Materials Science and Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway. ²Graphene Batteries AS, c/o SINTEF, 0134 Oslo, Norway. ³Morrow Batteries, Nye Apotekergata 10, 0180 Oslo, Norway.



intimate contact with the conductive carbon is required. Carbon coating of the LFP powder is common in order to improve the electronic conduction paths through the electrode. Similarly, processing parameters, like calendaring, are important for the performance of these cathodes [2].

In addition to good contact between particles, minimizing the contact resistance between the LFP/carbon conductive additive cathode and the current collector is important for the cycling performance. Illig et al. [3] demonstrated that a significant fraction of the overall polarization resistance could be attributed to the contact resistance at the interface between the cathode and the current collector, in particular at high state of charge (SOC). The contact resistance was responsible for around 50% of the total polarization at 50% SOC, and dominating at 100% SOC. In the study of Busson et al. [4], it was verified that with the use of carbon-coated aluminum collector (coating of 100 nm sized carbon particles via an ink solution with binder), combined with carbon-coated LFP, eliminated the need for addition of carbon conductive additives in the electrodes.

The use of carbon-coatings on current collectors has been reported to lower the contact resistance, and thus considerably improve the performance for a range of electrodes for various electrochemical energy storage systems. These include activated carbon electrodes, used in supercapacitors [5, 6], as well as for cathode materials for Li-ion batteries, like $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [7] and LiMn_2O_4 [8], and for sulphur cathodes in Li-sulphur batteries [9]. The application of the carbon coatings has been performed by coating of slurries containing a carbon powder [5, 7], or slurries containing carbon black and fine graphite in various ratios [9]. Alternatively, the carbon coating has been applied by thermal cracking of CH_4 at 600 °C in a chemical vapor deposition (CVD) process [6].

Shim et al. [10] demonstrated cells with excellent performance by using carbon-coated Al-foil current collectors (proprietary technique of Hydro-Québec) to develop low-cost lithium ion batteries with carbon coated LFP and natural graphite. However, in this work neither the effect of the carbon-coated collector, nor the method for application of the carbon coating, are shown. Striebel et al. [11] demonstrated improved rate performance, more stable cycling and a lower area-specific resistance (ASR) of LFP on carbon-coated current collectors compared to uncoated current collectors, when cycled in full cells with a graphite anode. The carbon coating was obtained by casting of the carbon black onto the foil with a PVDF binder. Similar findings were reported by Swain et al. [12] with a commercial carbon-coated current-collector (MTI-corporation, with acrylate binder). Wu et al. also demonstrated significantly improved rate performance and improved cycling stability for LFP cathodes deposited onto an etched and

carbon-coated aluminum current collector [13]. The carbon coating was obtained by cracking of CH_4 (600 °C) on etched foils. The improvements were explained in terms of a combined effect of reduction of the insulating aluminum oxide layer on the current collector by the etching, and the improved adhesion at the interface between LFP particles and the carbon-coating of the Al-foil.

Here, we demonstrate the significant reduction of contact resistance in LFP cathodes, fabricated from carbon-coated LFP powder, by the use of carbon-coated aluminum current collectors. The contact resistance is measured both in a 4-probe set-up, as well as indirectly by impedance spectroscopy, and the effect on the rate performance of LFP cathodes is reported. In contrast to previously reported carbon coated current collectors [4, 5, 7, 9, 11–13], the low cost carbon coating in this work was applied without the use of binders and solvents. Thus, introduction of non-active materials, and potentially degrading materials, are avoided in the cells. In the following sections, we start by providing the details for the experimental work (Sect. 2). In the next section, experimental results are presented, starting with the characterization of the carbon-coated foils (Sect. 3.1), ex-situ measurements of contact resistance comparing the coated and pristine aluminum foils (Sect. 3.2), and last a comparison the electrochemical performance of LFP cathodes applied onto coated or pristine foils, including also electrochemical impedance spectra (Sect. 3.3). Finally, the main findings are summarized in the conclusions (Sect. 4).

2 Experimental

Aluminium foil current collectors (25 μm from Gelon Lib, China) were used either as delivered, or in carbon-coated state. The carbon coating is solvent free (proprietary technology of Morrow Batteries). These foils are referred to as the *coated* current collectors in the text.

Raman spectra were recorded with a Jobin Yvon Horiba Labram using a He–Ne laser (632.5 nm) with a beam diameter of 100 μm of the coated current collectors. The following correlation as given in Ref. [14], was applied to determine the *in-plane* crystallite size, L_a of the carbon coating

$$L_a(\text{nm}) = \frac{560}{E_l^4} \left(\frac{I_D}{I_G} \right)^{-1} \quad (1)$$

where E_l is the laser excitation energy in the unit of eV.

A slurry composed of active material (86 wt% carbon-coated lithium iron phosphate, LiFePO_4 , Clariant Life Power®P2), binder (7 wt% polyvinylidene fluoride, Kynar) and conductive additives (7 wt% carbon black, Timcal Super P®) was prepared by mixing the

constituents together with n-methyl-2-pyrrolidone (NMP Sigma-Aldrich).

The slurry was tape casted onto the coated and uncoated current collectors with a doctor blade (active material mass loading was around 10 mg/cm^2 on both aluminium foils) before the electrode sheet was dried in two steps, first on the tape casting bed at 60°C for two hours and then in vacuum at 80°C overnight.

Electrode sheets were pressed at 5 tons with a 5.5 cm punch die, before cut to appropriate disc sizes, 14 mm or 16 mm in diameter for coin cells and 16 mm in diameter for the 3-electrode cell used for electrochemical impedance spectroscopy (EIS). The electrode discs were additionally dried in vacuum (80°C) upon introduction into an argon-filled glove box ($\text{O}_2 < 0.1 \text{ ppm}$, $\text{H}_2\text{O} < 0.1 \text{ ppm}$). The thickness of the pressed electrodes was around $40 (\pm 2) \mu\text{m}$, which gives an average porosity of around 20%, based on the density of the materials.

Rate capability of the electrodes were studied in half-cell configuration in 2032-type coin cells with a lithium foil (0.75 mm, Sigma-Aldrich) counter electrode and a Celgard®2400 separator. The electrolyte was 1 M Lithium Hexafluorophosphate (LiPF_6) in 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), based on weight. Electrodes extracted from A123 commercial LFP cells were used as reference, and are referred to as “commercial electrodes” in the text.

The cells were cycled in a Maccor 4200 test system at room temperature. All half-cells were charged (delithiated) and discharged in the voltage window of 2.5–4.0 V in a CCCV procedure, with constant current corresponding to 1C, 2C, 3C, 4C, 5C, 10C, 12C, 15C, 18C and 20C.

The interfacial contact resistance was determined using an in-house four-point contact test rig designed to measure through-sheet resistance [15]. A current of 2 A (Xantrex XDL 56-4P DC power supply) was used, and the contact resistance was determined from the measured voltage (Keithley 2000 multimeter) at different pressures.

Electrochemical Impedance Spectroscopy (EIS) measurements were conducted in Hohen HS-3E cell, with a glass fiber separator (Whatman Grade GF/A Glass Microfiber Filter), by use of a VMP-300 from Biologic Science Instruments. The amplitude was 5 mV, in the frequency range of 500 kHz to 10 mHz. Initially, all cells were cycled three times and left to rest at a predetermined 50% SOC. The cells were then disassembled and the cathodes were extracted and reassembled in a symmetrical cell configuration. The impedance data were further analyzed with MATLABs toolbox DRT-TOOLS to reveal distribution of relaxation times (DRT) based on Tikhonov regularization [16].

3 Results and discussion

3.1 Characterization of the carbon coating

The carbon coating applied on the current collectors is thin, and not visible in SEM. For the verification of the presence and the structure of the carbon coating, Raman spectroscopy is considered a viable technique. The Raman spectrum obtained for the coated aluminum collector is shown in Fig. 1. The spectrum shows a noticeable D-band, associated with vibrational modes present at defects and edge planes of the carbon ($\sim 1330/\text{cm}$), less prominent G-band, resulting from the sp^2 bonds ($\sim 1595/\text{cm}$) and a weak 2D band ($\sim 2658/\text{cm}$). In addition, a D'-band ($\sim 1607/\text{cm}$) is present on the shoulder of the G-band. The D'-bands observed is most likely reflecting modes at the edge planes of hexagonal carbon layers. The 2D band is a second-order overtone resulting from different interlayer interactions. The dominating D-peak reveals a low the degree of graphitization and a high amount of disordered carbon in the sample. Raman spectroscopy is a well-known technique for determination of the average *in-plane* crystallite size of graphite, L_a . It was first demonstrated by Tuinstra and Koenig [17] that the ratio of the D and G band intensities (I_D/I_G) is inversely proportional to L_a . The correlation has been developed further for nanographite [14], taking into account also effects of excitation energy, as given by Eq. (1). For the carbon coating applied to our samples, this results in a value of L_a of 16 nm.

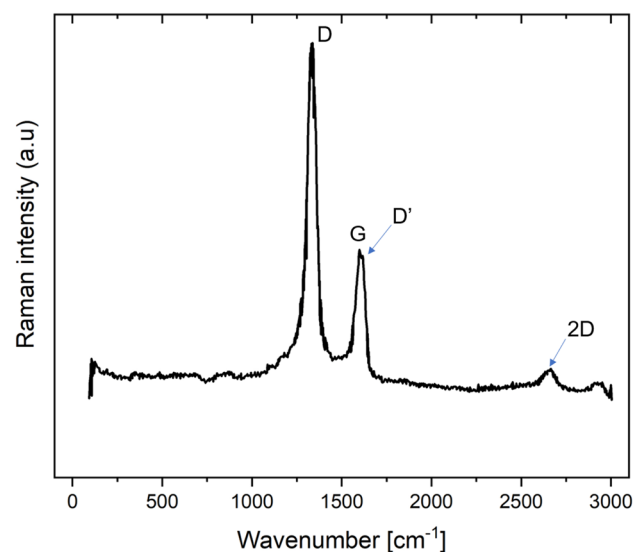


Fig. 1 Raman spectrum obtained for the carbon-coated aluminum current collector

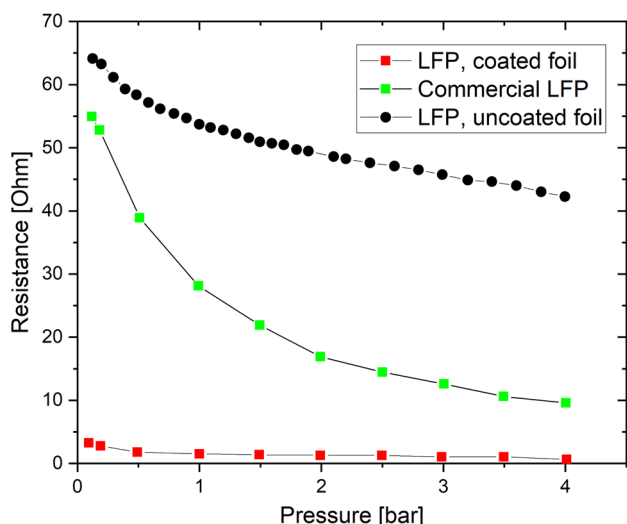


Fig. 2 Through-sheet resistance of dry, sandwiched electrodes with and without coating, and a commercial LFP cathode, as a function of pressure

3.2 Assessment of the contact resistance

The measured contact resistance as a function of applied pressure of LFP cathode made from coated and uncoated current collectors, as well as one commercial electrode is shown in Fig. 2. The decreasing contact resistance with increasing pressure is expected, and related to the compressibility and elastic behavior of the porous electrode. As seen from Fig. 2, there is a dramatic reduction of the contact resistance for the carbon-coated electrode.

3.3 Electrochemical performance of LFP cathodes

Figure 3a) shows the results of the rate performance tests of coated and uncoated current collectors, conducted in a half cell configuration. As seen from Fig. 3a), electrodes deposited on coated current collectors have the ability to maintain 89% of the initial discharge capacity at the high rate of 5C, which is significantly higher than the capacity obtained for the cathodes on uncoated foils. While the LFP cathode on uncoated foils fail to deliver any capacity at 10C and above, the LFP on coated foils can deliver a capacity of around 80 mAh/g at the high rate of 12C. These results are superior to previously reported results. Striebel et al. [11], for instance, reported capacities of 140, 130 and 20 vs. 160, 130 and 110 mAh/g, for LFP electrodes (area specific capacity of around 0.83 mAh/cm²) on uncoated and coated foils cycled in half cell configuration at 1C, 2C and 5C, respectively. Wu et al. [13] studied electrodes of low loading (2.5 mg/cm²), and reported 100 and 70 vs. 120 and 110 mAh/g for LFP electrodes on uncoated and coated foils, cycled in half cell

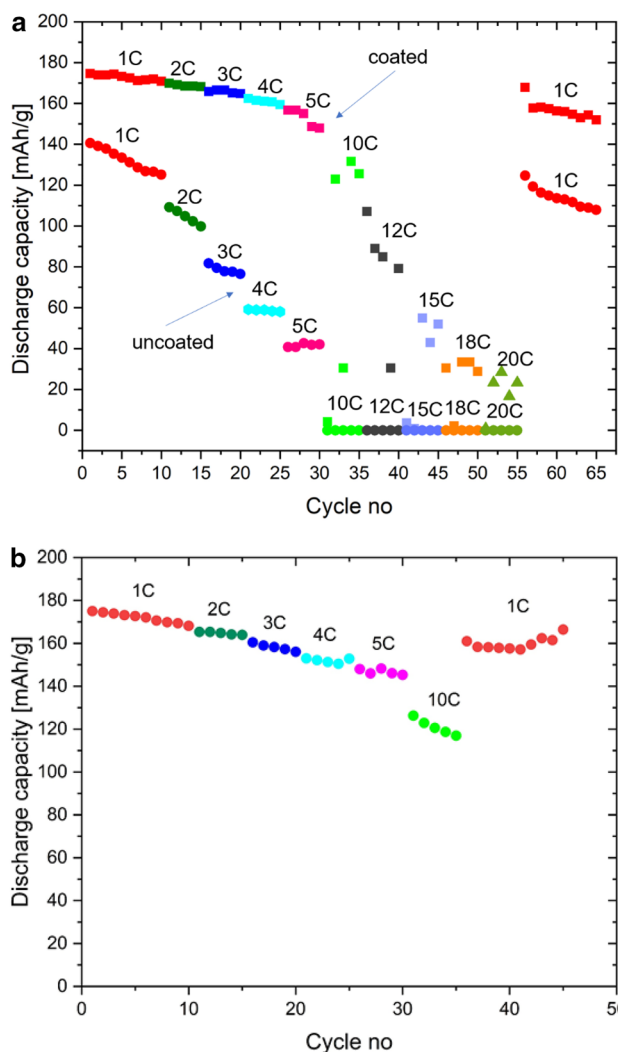


Fig. 3 a Discharge capacities of LFP cathodes with carbon-coated current collector, and uncoated current collector, measured at different C-rates in the voltage window 2.5–4 V. **b** Discharge capacities of LFP cathodes with carbon-coated current collector measured at different C-rates in the voltage window 2.5–4 V at a temperature of 60 °C

configuration at 1C and 5C. The LFP powder used for this specific study was not carbon coated. In the study of Busson et al. [4], the experimental matrix was expanded to include also effects of wt% carbon conductive additives in the cathodes of carbon-coated LFP (1.7 mAh/cm²). Their results from full-cell experiments showed that with a sufficiently high content of carbon black, the cells delivered very similar capacities for coated and uncoated aluminum foils (around 120 mAh/g with respect to the LFP active material), but with a reduced polarization for the coated foils. For electrodes with a reduced content of the carbon black, the effect of carbon coating on the aluminum current collector was significant.

Figure 3b) shows the discharge capacities obtained for LFP on coated aluminium foils at C-rates up to 10C, at a temperature of 60 °C. The good performance at the elevated temperature is taken as an indication of a reasonably durable coating. In order to investigate possible side reactions occurring on the carbon-coated foils, cyclic voltammetry was conducted at a low rate (0.1 mV/s) in the voltage range 3–4 V. The current densities observed are below 5 $\mu\text{A}/\text{cm}^2$ in this voltage range, and no peaks are observed (for comparison, the currents observed on pristine Al foils were below 1 $\mu\text{A}/\text{cm}^2$).

The EIS data are shown in Nyquist representation for the LFP cathodes on uncoated Al-foil in Fig. 4a). The corresponding Nyquist plot for the LFP cathode in coated Al-foil is shown in Fig. 4b), while the distribution of relaxation times (DRT), known to be more sensitive to identification

of individual processes, determined in accordance with Schmidt et al. [18], is shown in Fig. 4c). In line with the rate performance results shown in Fig. 3, a significant decrease of the electrode resistance for the electrode on the coated foil is observed in Fig. 4b). In fact, the apparent electrode resistance obtained with the uncoated foil has a significant contribution from the interfacial contact resistance, which is also consistent with the DC contact resistance measurements shown in Fig. 2, and in agreement with results reported in Illig et al. [3], where at 50% SOC, the electrode resistance of LFP electrodes was similar in magnitude as the interfacial contact resistance to the current collector.

For the distribution of relaxation times (DRT), two distinct peaks at 0.01 Hz and 1500 Hz are visible for uncoated electrodes (stippled line), while the coated electrode produce only one peak at 0.01 Hz (the diffusion impedance

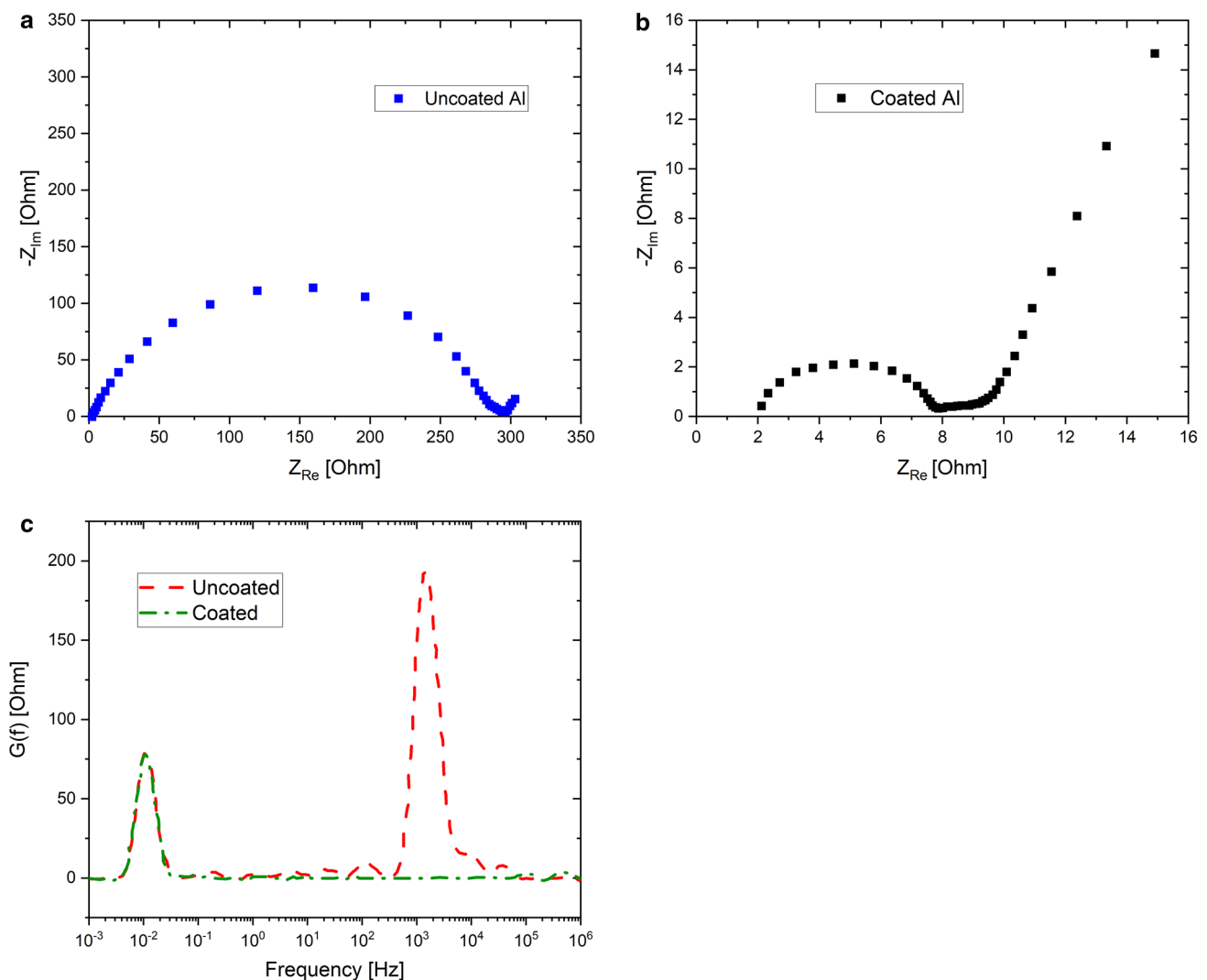


Fig. 4 Electrochemical impedance spectra of a symmetrical cell of LFP cathodes at 50% SOC, on **a** uncoated foils. **b** coated foils, and **c** the distribution of relaxation times, $G(f)$, derived from the impedance spectra of cells with coated and uncoated electrodes

dominating at the lowest frequencies is not included in the analysis). Since the electrodes are practically identical, except for the coated/uncoated current collector, it is believed that the origin of the 1500 Hz-peak comes from the increased resistance between the active material and current collector. The low frequency peak most likely originates from the charge transfer between the electrolyte and the active material, which will be present for electrodes regardless of the coating on the current collectors, as has also been pointed out in other works [3, 18].

4 Conclusion

In this study, a novel, binder-free carbon coating has been demonstrated for aluminum current collectors for Li-ion battery cathodes, and verified to significantly reduce the interfacial contact resistance in combination with cathode fabricated from carbon-coated LFP. Excellent rate performance was demonstrated with the cathodes made with this current collector, with a capacity retention of 89% at 5C. Similarly, a significant reduction of the electrode resistance was verified by electrochemical impedance spectroscopy. With the uncoated current collectors, the impedance response was dominated by the interfacial contact, while effects of the interfacial contact resistance were practically eliminated with the carbon-coated current collectors. Overall, the results show great promise for improving the performance of LFP cathodes, provided that the coating procedure can be upscaled for industrial applications. The coated current collectors should also be verified in combination with other active materials, like activated carbon, other Li-ion cathode materials, or sulphur in the future.

Funding Open access funding provided by Norwegian University of Science and Technology. The authors would like to thank the Research Council of Norway for the financial support of the research, under the Contract no. 245460.

Data availability All results shown in this manuscript are available upon request.

Declarations

Conflict of interest The co-author SF is an employee of the company Morrow Batteries. The procedure for application of the carbon coating is a proprietary process of Morrow Batteries.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this

article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. Padhi AK, Nanjundaswamy KS, Goodenough JB (1997) Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J Electrochem Soc* 144:1188–1194. <https://doi.org/10.1149/1.1837571>
2. Van Bommel A, Divigalpitiya R (2012) Effect of calendaring LiFePO₄ electrodes. *J Electrochem Soc* 159:A1791–A1795. <https://doi.org/10.1149/2.029211jes>
3. Illig J, Ender M, Chrobak T, Schmidt JP, Klotz D, Ivers-Tiffée E (2012) Separation of charge transfer and contact resistance in LiFePO₄-cathodes by impedance modeling. *J Electrochem Soc* 159:A952–960. <https://doi.org/10.1149/2.030207jes>
4. Busson C, Blin M-A, Guichard P, Soudan S, Crosnier O, Guyomard D, Lestriez B (2018) A primed current collector for high performance carbon-coated LiFePO₄ electrodes with no carbon additive. *J Power Sources* 406:7–17. <https://doi.org/10.1016/j.jpowsour.2018.10.018>
5. Portet C, Taberna PL, Simon P, Laberty-Robert C (2004) Modification of Al current collector surface by sol–gel deposit, for carbon–carbon supercapacitor applications. *Electrochim Acta* 49:905–912. <https://doi.org/10.1016/j.electacta.2003.09.043>
6. Wu H-C, Lin YP, Lee E, Lin WT, Hu JK, Chen HC, Wu NL (2009) High-performance carbon-based supercapacitors using Al current-collector with conformal carbon coating. *Mater Chem Phys* 117:294–300. <https://doi.org/10.1016/j.matchemphys.2009.06.001>
7. Bizot C, Blin M-A, Guichard P, Soudan P, Gaubicher J, Poizot P (2021) Aluminum current collector for high voltage Li-ion battery. Part II: benefit of the En' Safe® primed current collector technology. *Electrochem Commun* 126:107008. <https://doi.org/10.1016/j.elecom.2021.107008>
8. Hjelm A-K, Lindbergh G (2002) Experimental and theoretical analysis of LiMn₂O₄ cathodes for use in rechargeable lithium batteries by electrochemical impedance spectroscopy (EIS). *Electrochim Acta* 47:1747–1759. [https://doi.org/10.1016/S0013-4686\(02\)00008-7](https://doi.org/10.1016/S0013-4686(02)00008-7)
9. Li T, Bo H, Cao H, Lai Y, Liu Y (2017) Carbon-coated aluminum foil as current collector for improving the performance of lithium sulfur batteries. *Int J Electrochem Sci* 12:3099–3108. <https://doi.org/10.20964/2017.04.20>
10. Shim J, Striebel KA (2003) Cycling performance of low-cost lithium ion batteries with natural graphite and LiFePO₄. *J Power Sources* 119–121:955–958. [https://doi.org/10.1016/S0378-7753\(03\)00297-0](https://doi.org/10.1016/S0378-7753(03)00297-0)
11. Striebel K, Shim J, Sierra A, Yang H, Song X, Kostecky R, McCarthy K (2005) The development of low cost LiFePO₄-based high power lithium-ion batteries. *J Power Sources* 146:33–38. <https://doi.org/10.1016/j.jpowsour.2005.03.119>
12. Swain P, Viji M, Mocherla PSV, Sudakar P (2015) Carbon coating on the current collector and LiFePO₄ nanoparticles—influence of sp² and sp³-like disordered carbon on the electrochemical properties. *J Power Sources* 293:613–625. <https://doi.org/10.1016/j.jpowsour.2015.05.110>

13. Wu H-C, Wu H-C, Lee E, Wu N-L (2010) High-temperature carbon-coated aluminum current collector for enhanced power performance of LiFePO_4 electrode of Li-ion batteries. *Electrochem Commun* 472:488–491. <https://doi.org/10.1016/j.elecom.2010.01.028>
14. Cançado LG, Takai K, Enoki T (2006) General equation for determination of the crystallite size L_a of nanographite by Raman spectroscopy. *Appl Phys Lett* 88:163106
15. Lædre S, Kongstein OE, Ødegaard A, Karoliussen H, Seland F (2017) Materials for Proton Exchange Membrane water electrolyzer bipolar plates. *Int J Hydrogen Energy* 42(5):2713–2723. <https://doi.org/10.1016/j.ijhydene.2016.11.106>
16. Wan TH, Saccoccio M, Chen C, Ciucci F (2015) Influence of the discretization methods on the distribution of relaxation times deconvolution: implementing radial basis functions with DRTtools. *Electrochim Acta* 184:483–499. <https://doi.org/10.1016/j.electacta.2015.09.097>
17. Tuinstra F, Koenig JL (1970) Raman spectrum of graphite. *J Chem Phys* 53:1126–1130
18. Schmidt JP, Chrobak T, Ender M, Illig J, Klotz D, Ivers-Tiffée E (2011) Studies on LiFePO_4 as cathode material using impedance spectroscopy. *J Power Sources* 196:5342–5348. <https://doi.org/10.1016/j.jpowsour.2010.09.121>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.