Available online at www.sciencedirect.com

ScienceDirect

Procedia CIRP 42 (2016) 433 – 438

www.elsevier.com/locate/procedia

18th CIRP Conference on Electro Physical and Chemical Machining (ISEM XVIII)

Quality and Productivity Considerations for Laser Cutting of $LiFePO_4$ and $LiNiMnCoO_2$ Battery Electrodes

Adrian H.A. Lutey[a,]*, Alessandro Fortunato[a], Simone Carmignato[b], Alessandro Ascari[a], Erica Liverani[a], Giacomo Guerrini[a]

[a]*DIN, Università di Bologna, viale Risorgimento 2, Bologna 40136, Italy*
[b]*DTG, Università degli Studi di Padova, Stradella San Nicola 3, Vicenza 36100, Italy*

* Corresponding author. Tel.: +39-051-20-90525; *E-mail address:* adrian.lutey2@unibo.it

Abstract

Laser cutting of lithium-ion battery electrodes has been shown to be a viable alternative to mechanical blanking for some specific electrode types, yielding similar cut quality and throughput but with decreased on-going costs due to lower maintenance requirements. The multitude of electrode chemistries within the lithium-ion classification, particularly with regards to the cathode, together with the sensitive nature of battery components such as the polymeric separator films and electrodes themselves, requires careful assessment of defects for each electrode type. In the present work, cutting of $LiNiMnCoO_2$ (LNMC) coated aluminium cathodes and graphite coated copper anodes is performed at 100 mm/s with a 1064 nm pulsed fibre laser with 25 µm spot size, varying the pulse duration, energy and repetition rate over the ranges 4-200 ns, 8-935 µJ and 20-500 kHz, respectively. Process productivity is assessed in terms of the minimum cutting power at which complete electrode penetration takes place. A scanning electron microscope is utilised to assess upper coating layer clearance width and to determine the presence and dimensions of defects resulting from melting of the coating layers. Results are compared with previous cuts performed on $LiFePO_4$ (LFP), with differences observed in the parameters leading to minimum average cutting power and optimum quality between cathode types. Laser pulse fluence in the range 35-40 J/cm^2 with 30 ns pulse duration and 100 kHz repetition rate is found to lead to the highest cutting efficiency and quality for the LFP cathode, while 110-150 J/cm^2 fluence with 200 ns pulse duration and 20 kHz repetition rate is instead found to be ideal for the LNMC cathode and for the anode. The present on-going study indicates relatively strong sensitivities to electrode composition and laser pulse fluence for cutting efficiency and quality.

Peer-review under responsibility of the organizing committee of 18th CIRP Conference on Electro Physical and Chemical Machining (ISEM XVIII)

Keywords: Li-ion; Electrodes; Laser Cutting; Ablation; $LiFePO_4$; $LiNiMnCoO_2$

1. Introduction

Present-day outlook for li-ion battery applications in automotive, portable electronics and stationary storage sectors requires the use of production technologies that can provide high quality at the lowest possible cost [1,2]. Current plans to massively increase global battery production for emerging products, in particular electric vehicles (EVs) [3,4], creates opportunities for investment into manufacturing techniques that rely on high volume throughput to improve economic viability. Laser cutting of battery electrodes is one such technology, where the non-contact nature of pulsed laser irradiation avoids costs and technical difficulties associated with tool wear in mechanical blanking [5]. Previous studies have shown that pulsed laser cutting can result in lower costs than those associated with mechanical blanking after as little as two years of high-volume production [6]. The thermal nature of laser-material interactions and the sensitivity of electrode films to the process parameters utilized, however, necessitate detailed investigation into the effects of laser irradiation on cut quality and efficiency for each specific case.

Li-ion chemistries with $LiFePO_4$ (LFP) and $LiNiMnCoO_2$ (LNMC) cathodes are currently of particular relevance to global markets. The former offers superior thermal stability and cycle life while the latter provides excellent specific energy [7]. Electrode films are typically 100-150 µm in thickness, with cathodes comprising aluminium conductor films coated on both sides with LFP or LNMC and anodes

Peer-review under responsibility of the organizing committee of 18th CIRP Conference on Electro Physical and Chemical Machining (ISEM XVIII)
doi:10.1016/j.procir.2016.02.227

comprising copper conductor films coated on both sides with polycrystalline graphite.

Pulsed laser exposure of thin multi-layer films involves ablation of material directly exposed to the laser beam during each laser pulse, together with longer-term temperature rise and thermal conduction due to heat accumulation over several consecutive pulses. The ablation thresholds of the electrode component materials are very diverse due to their contrasting physical properties; the active layers exhibit high optical absorptivity, low thermal conductivity and relatively low melting and vaporisation temperatures, while the metallic conductor films are both reflective and conductive with elevated melting and vaporisation temperatures [6]. As a result, the ablation thresholds of the metallic layers are typically at least one order of magnitude higher (5.2 J/cm^2 for aluminium and 5.5 J/cm^2 for copper with 5 ns and 4.5 ns pulses, respectively [8,9]) than those of the active layers (approximately 0.5 J/cm^2 [6]) and are more sensitive to pulse duration. Laser pulse fluence must therefore be maintained above the metallic layer threshold to ensure complete film penetration via ablation. Heat accumulation and lateral heat conduction within the metallic layer lead to lateral heating of the active layers and development of the heat affected zone (HAZ), which must be minimised to ensure acceptable cut quality.

A number of studies have investigated continuous-wave and pulsed laser cutting of li-ion battery electrodes in terms of minimum average cutting power and chemical changes for specific cases [10,11]. A detailed investigation into the effects of laser pulse duration, repetition rate and laser pulse fluence for LFP electrodes was recently presented by the authors [6]; however, there continues to be scope for detailed studies into the impact of process parameters on laser cutting of LNMC electrodes. Given the strong dependence of laser cutting efficiency and quality on process parameters for other electrode types, optimisation for LNMC represents a step forward in improving the battery production process, reducing cell costs and improving reliability.

The present paper sees laser exposures performed on LNMC battery electrodes with a nanosecond pulse fibre laser while varying the pulse duration, repetition rate and laser pulse fluence. For each combination of parameters, minimum average cutting power is determined and cut quality is assessed via scanning electron microscopy. Results for LNMC are compared to those previously obtained for LFP, yielding insight into the sensitivity of laser cutting to electrode chemical composition. The presented results provide new guidelines for optimisation of laser cutting parameters in high throughput battery production facilities.

2. Experimental setup

2.1. Laser and sample mounting

An IPG YLPM-1-4 200-20-20 1064 nm nanosecond pulsed fibre laser equipped with galvanometric scanning head was employed for the experiments. The laser exhibited a beam quality factor of $M^2 = 1.5$, with a 100 mm focal length lens achieving a 25 µm Gaussian spot diameter and 320 µm Rayleigh range. Attainable pulse duration, energy and repetition rate ranges were 4-200 ns, 8-935 µJ and 20-500 kHz, respectively, with limitations on the minimum pulse duration attainable at high pulse energy. Three parameter groups were utilised for the experiments (Table 1) with low, moderate and high laser pulse fluence, respectively, and repetition rates chosen to achieve comparable average beam power.

Table 1. Laser parameters employed for the experiments. *Pulse overlap has been calculated as the Gaussian intensity overlap of consecutive laser pulses in the cut direction with a Gaussian beam diameter of 25 µm.

Parameter group	1	2	3
Pulse duration (ns)	4	30	200
Repetition rate (kHz)	500	100	20
Max. average power (W)	19	18.8	18.7
Max. pulse energy (µJ)	38	188	935
Max. laser pulse fluence (J/cm^2)	15	74	369
Pulse overlap* @ 100 mm/s (%)	98.7	93.6	68.9

2.2. Test samples

Cathode and anode films were 150 µm and 110 µm thick nominally. The cathode comprised a 20 µm aluminium conductor film coated on both sides with LNMC and the anode a 10 µm copper conductor film coated on both sides with polycrystalline graphite. Schematic cross-sections of the films are presented in Figure 1.

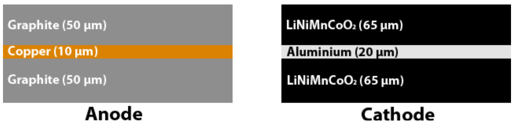

Figure. 1. Schematic cross-sections of electrode films.

2.3. Experimental procedure

Rectangular laser exposures, 40 mm x 3 mm in form, were performed on the electrode films at 100 mm/s with the galvanometric scanning head. For each parameter group, the average laser power was varied from 20 % to 100 % at intervals of 10 %. Electrode films were mounted on a vacuum table with cut-outs below the exposed area to avoid contact between the film and table in the exposed area. A photograph of the experimental setup is provided in Figure 2.

2.4. Measurements

Minimum average cutting power was determined for each electrode type and parameter group as the minimum average power at which uninterrupted film penetration took place over at least 5 mm of the exposed path. In some cases, such parameters did not lead to complete separation of the rectangular cut-out due to laser beam instability (< 5 %) and small variations in electrode film thickness and vertical positioning. Such a response, however, was only observed at the very onset of complete film penetration.

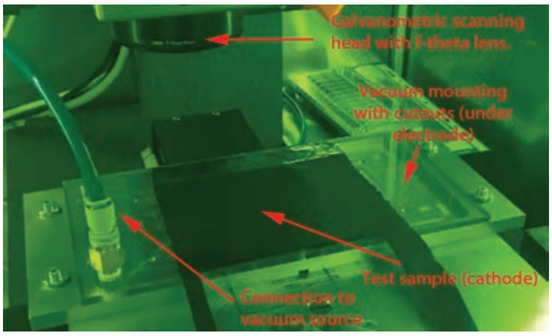

Figure. 2. Photograph of experimental setup.

Cut edges were analysed via scanning electron microscopy for exposures performed with 10 % greater laser power than the minimum average cutting power for each parameter group. Such a scenario was considered realistic for industrial settings where laser parameters would be chosen to ensure complete separation of cut edges in all cases.

3. Results and discussion

3.1. Minimum average cutting power

The minimum average cutting power and corresponding laser pulse fluence for the electrode films subject to all parameter groups are presented in Figure 3, together with values observed in a previous study for LFP cathode films under the same cutting conditions [6]. Comparing the values for LNMC and LFP, it is evident that the lowest average cutting power is achieved with higher laser pulse fluence and lower repetition rate for LNMC than for LFP. A repetition rate of 20 kHz and laser pulse fluence of approximately 110 J/cm^2 leads to highest cutting efficiency for LNMC, while a repetition rate of 100 kHz and fluence of approximately 35-40 J/cm^2 leads to highest cutting efficiency for LFP. As the conductor film is the same in both cases, this result may be due to greater shielding effects by the LNMC ablation products at very high pulse overlap, or strong shielding effects by the LFP ablation products at very high fluence. In either case, these results have implications for the ideal parameter ranges for cutting cathode films. Parameter group 3 leads to lowest average cutting power for the anode with a repetition rate of 20 kHz and laser pulse fluence of approximately 150 J/cm^2. Such high fluence is required in this case due to the elevated ablation threshold of the copper conductor film.

It may be seen that the repetition rate and laser pulse fluence are of greater influence on the minimum average cutting power than the pulse duration over the tested range. While a shorter pulse is expected to improve ablation efficiency due to a reduction in heat conduction losses during individual pulses [12], it is evident that laser pulse fluence and overlap are of greater importance in optimising material ejection volume and reducing shielding effects by the ablation products. An investigation into shorter pulse durations at moderate and high fluence with a different laser source presents scope for future studies.

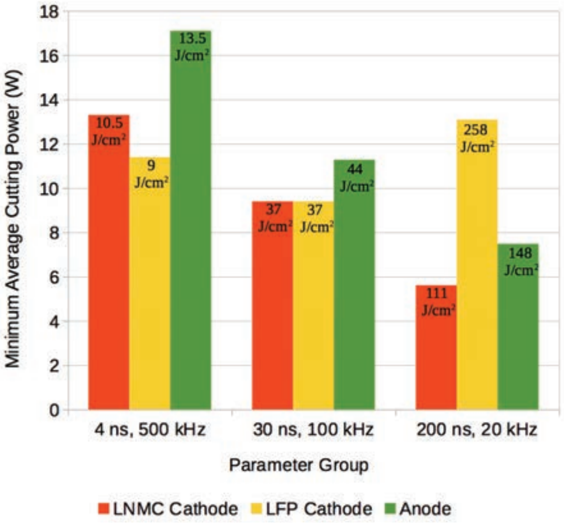

Figure. 3. Minimum average cutting power and corresponding pulse fluence at 100 mm/s for the LNMC cathode, LFP cathode and graphite anode.

The implications of these results are important from both efficiency and economic points of view, as correct selection of laser parameters can more than halve the average laser power required to achieve complete film penetration. Minimum average cutting power for the LNMC electrodes with parameter group 1 is more than twice that required with parameter group 3. It is also clear that ideal parameter ranges are strongly dependent on cathode composition, for which the same cutting parameters are not necessarily appropriate for all cathode types. This is particularly evident with parameter group 3, where values for the two cathode types diverge; LNMC requiring lower average power than for group 2 and LFP requiring greater.

3.2. SEM analysis

SEM images of the resulting cut edges following laser exposure are presented in Figures 4-6 for the LNMC cathode, LFP cathode and graphite anode, respectively. All cut edges exhibit a visible clearance width, where the upper coating layer is removed over a larger width than the metallic conductor layer, leaving a section exposed. This characteristic may be the result of two phenomena: direct ablation of the upper coating layer over a larger width than the underlying metallic layer due to differences in ablation threshold, or heat accumulation and conduction effects from the metallic layer leading to subsequent heating and removal of the active layer beyond the exposed area. The latter is more likely in the present case due to the presence of clearance widths that are larger than the focused spot radius.

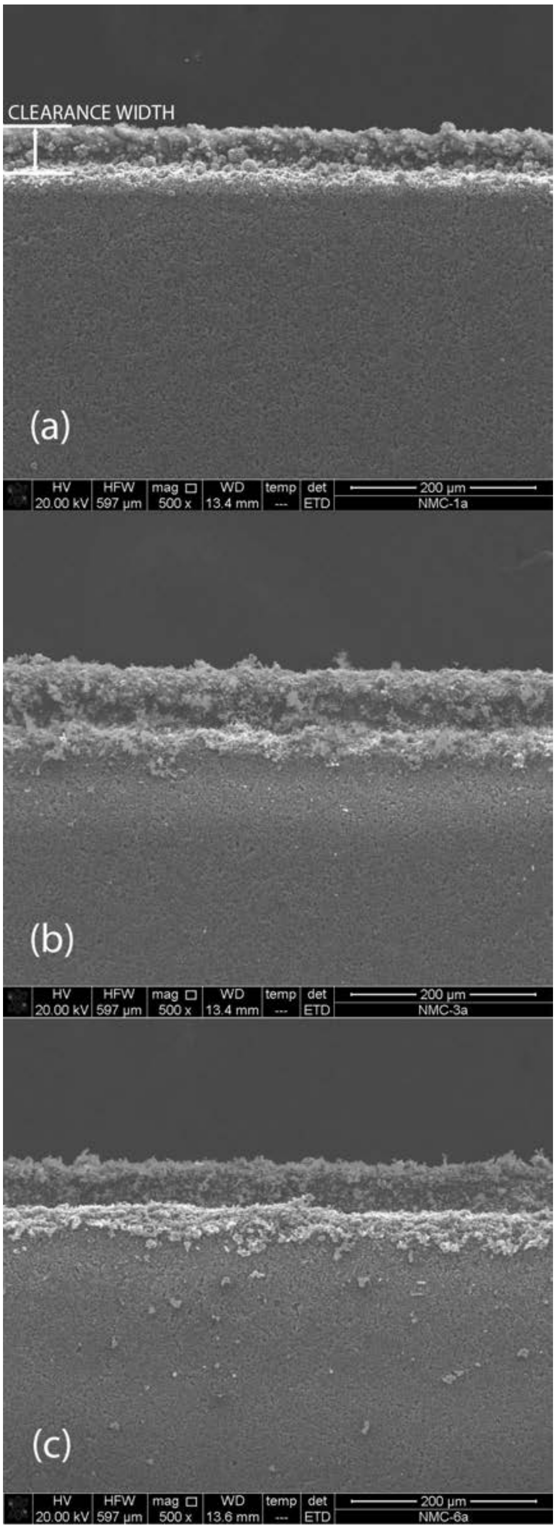

Figure. 4. SEM image of LNMC cathode cut edges following exposure to parameter groups (a) 1, (b) 2 and (c) 3.

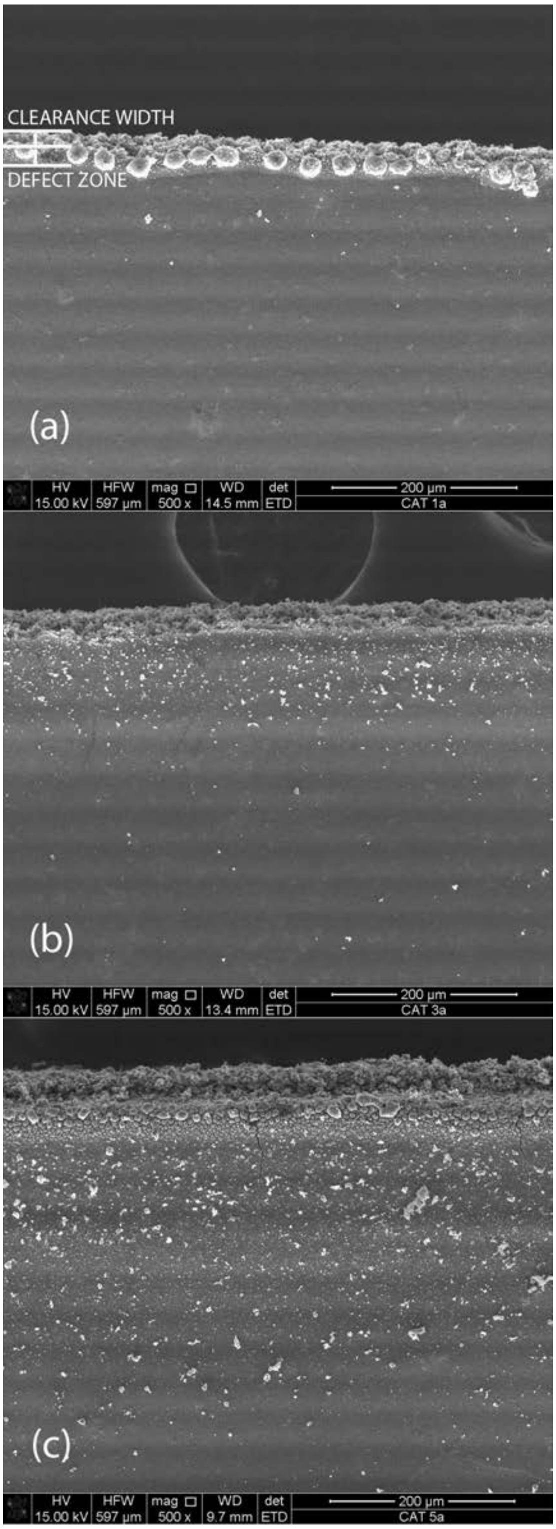

Figure. 5. SEM image of LFP cathode cut edges following exposure to parameter groups (a) 1, (b) 2 and (c) 3.

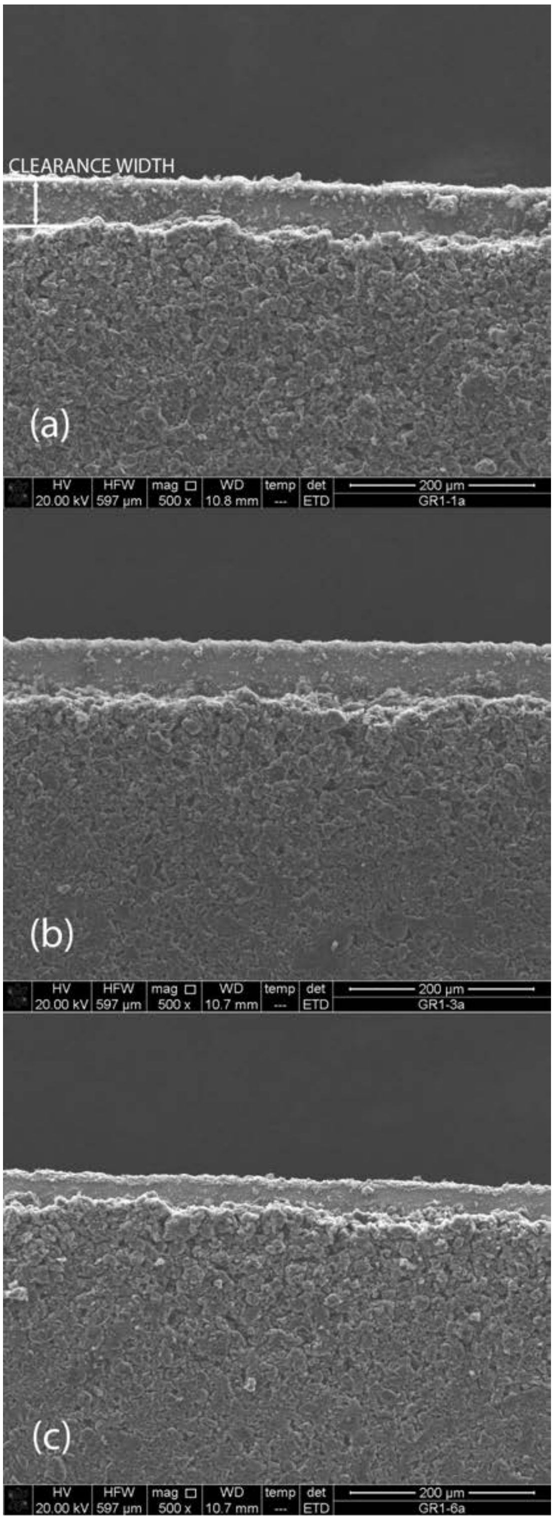

Figure. 6. SEM image of graphite anode cut edges following exposure to parameter groups (a) 1, (b) 2 and (c) 3.

Comparing the two cathode materials, LFP displays greater sensitivity to process parameters than does LNMC. With parameter group 1, evidence of active layer melting and resolidification is present along the cut edge for LFP in the form of spherical defects approximately 25 µm in diameter. For group 3, smaller spherical defects are visible with some cracking of the coating layer, while with group 2 no such formations or cracking are present. The clearance width is similar for groups 1 and 2, 20-25 µm, and slightly larger for group 3. There is a link between macroscopic cut quality and minimum average cutting power, as highest visible quality is attained with group 2, the same parameters with which the average cutting power is minimised. Melting of the active coating layer is therefore the result of greater heat accumulation in cases where cutting efficiency is lower.

No such spherical defects are visible along the cut edge for the LNMC cathode; however, clearance widths are larger than for LFP, in the range 30-50 µm. Highest visible cut quality is attained with parameter group 1, where average cutting power is maximum. Though this electrode appears to exhibit lower sensitivity to laser parameters than LFP in terms of macroscopic cut quality, cleaner cut edges result from exposure with pulses of lower fluence, despite the lower observed cutting efficiency in Figure 3. An investigation into chemical and microstructural changes with high and low laser pulse fluence is necessary to determine the effects of heat accumulation under these conditions.

The anode cut edge exhibits similar characteristics to those of the LNMC cathode, with minimal macroscopic defects. As with the LFP cathode, highest visible quality is attained with the same parameters that minimise average cutting power. In this case, both average cutting power and clearance width are minimised with parameter group 3. Removal of the active coating layer near the cut edge is therefore the result of heat accumulation.

4. Conclusion and outlook

The present paper has indicated some of the underlying factors influencing laser cutting efficiency and quality for multi-layer LNMC and LFP electrode films. Minimum average cutting power and cut edge quality have been found to be strongly dependent on laser pulse fluence and repetition rate over the tested parameter range, with minimum average cutting power more than doubling in some cases compared to that required with the optimum parameters. LNMC cathodes and polycrystalline graphite anodes require lowest average cutting power with a repetition rate of 20 kHz and laser pulse fluence in the range 110-150 J/cm^2, while LFP cathodes require lowest power with a repetition rate of 100 kHz and fluence of 35-40 J/cm^2. Cut quality for LFP cathodes is more strongly dependent on process parameters than the other tested electrodes, with highest quality coinciding with highest cutting efficiency.

Though results in the present work have been obtained at a cutting speed of 100 mm/s, insufficient for high throughput applications, the average laser power and repetition rate can be scaled proportionally to the velocity so as to maintain constant laser pulse fluence and overlap. Previous studies have shown that increasing the velocity in this way reduces heat conduction power losses and associated defects. Further quality improvements may also be obtained by utilising ultrashort pulses in the picosecond or femtosecond ranges. Final cutting speed must be calculated based on the electrode size and required throughput; however, speeds of at least 1 m/s are necessary to compete with existing mechanical blanking machines. Verification of cutting efficiency and quality at velocities of 1 m/s and greater is therefore necessary, together with a detailed study into microstructural and chemical changes following laser exposure. The present study has nonetheless indicated the ideal laser parameter ranges for maximum cutting efficiency and quality in what is an important emerging manufacturing market.

Acknowledgements

The authors would like to thank SOLITH, SOVEMA S.p.A. for provision of the electrode samples necessary for completion of this work.

References

[1] Burns JC, Kassam A, Sinha NN, Downie LE, Solnickova L, Way BM, Dahn JR. Predicting and extending the lifetime of li-ion batteries. J Electrochem Soc 2013;160:A1451-6.

[2] Scrosati B, Garche J. Lithium batteries: status, prospects and future. J Power Sources 2010;195:2419-30.

[3] Martin C. Driving change in the battery industry. Nature Nanotech 2014;9:327-8.

[4] Pollet BG, Staffell I, Shang JL. Current status of hybrid, battery and fuel cell electric vehicles: from electrochemistry to market prospects. Electrochim Acta 2012;84:235-49.

[5] Luetke M, Franke V, Techel A, Himmer T, Klotzbach U, Wetzig A, Beyer E. A comparative study of cutting electrodes for batteries with lasers. Phys Procedia 2011;12B:286-91.

[6] Lutey AHA, Fortunato A, Ascari A, Carmignato S, Leone C. Laser cutting of lithium iron phosphate battery electrodes: characterization of process efficiency and quality. Opt Laser Technol 2015;65:164-74.

[7] Eddahech A, Briat O, Vinassa J-M. Performance comparison of four lithium-ion battery technologies under calendar aging. Energy 2015;84:542-50.

[8] Porneala C, Willis DA. Time-resolved dynamics of nanosecond laser-induced phase explosion. J Phys D: Appl Phys 2009;42:155503.

[9] Vladoiu I, Stafe M, Negutu C, Popescu IM. The dependence of the ablation rate of metals on nanosecond laser fluence and wavelength. J Optoelectron Adv Mater 2008;10:3177.

[10] Lee D, Patwa R, Herfurth H, Mazumder J. Computational and experimental studies of laser cutting of the current collectors for lithium-ion batteries. J Power Sources 2012;210:327-38.

[11] Kronthaler MR, Schloegl F, Kurfer J, Wiedenmann R, Zaeh MF, Reinhart G. Laser cutting in the production of lithium ion cells. Phys Procedia 2012;39:213-24.

[12] Bovatsek J, Tamhankar A, Patel RS, Bulgakova NM, Bonse, J. Thin film removal mechanisms in ns-laser processing of photovoltaic materials. Thin Solid Films 2010;518:2897-904.