

Fire Risk Evaluation of the Internal Components of the Li-Ion Batteries

Sofia Ubaldi^a, Cinzia Di Bari^b, Paola Russo^{a,*}

^aDipartimento Ingegneria Chimica Materiali Ambiente, Sapienza Università di Roma, Via Eudossiana 18, Roma, 00185, Italy

^bENEA TERIN-DEC-MOST, CR Casaccia, Rome, Italy

paola.russo@uniroma1.it

The advantages of Lithium-ion batteries (LIBs) are well known, anyway the LIBs are even considered hazardous products. In fact, outside the safety windows the Li-ion cells can undergo to an abuse that leads to the degradation of the internal components with the release of gases, vapour, and solid products. The reactivity of the LIBs and the relative products composition is strictly correlated to the chemical composition of the internal components. Because of a lack of regulation, safety data sheets (SDS) of Li-ion cells are not mandatory but, generally they are available. However, there is a gap between the information reported in the SDS and the internal chemical composition, and usually the quantity of components is expressed as a range of weight percentages, and the chemical composition is not well specified. The most common lack of information concerns the electrolyte, which is usually defined as a mixture of organic carbonates without reporting the type of solvents (e.g., dimethyl carbonate, diethyl carbonate, and ethylene carbonate), the ratio between these components, and possible additives. The aim of this work was to characterize the internal components of various cylindrical 18650 cells available on the market, i.e., cell with Lithium Nickel Cobalt Aluminium Oxide (NCA) as cathode and graphite (C) or Lithium Titanate Oxide (LTO) as anode, and cells with Lithium Iron Phosphate (LFP) as cathode and C as anode. For this purpose, the cells were disassembled in a glovebox filled with argon (O_2 and $H_2O \leq 0.1$ ppm) and then the different components were analysed by various techniques to define their chemical composition, i.e., metals of the electrodes by ICP-OES, the electrolyte by GC-FID and SPME-GC-MS, and the separator by ATR-FT-IR and DSC. The identification of those compounds is fundamental to understand the reactions occurring inside the cells and to evaluate the risks for human health and environment.

1. Introduction

The principal advantages of Lithium-ion batteries (LIBs) are the high power density, high energy density, and high number of cycles. Anyway, due to the energy content, defined by the State of Charge (SoC), and the internal chemical composition the LIBs are even classified as hazardous products (Qiu et al., 2022). The LIBs are generally composed by four main components: anode, cathode, electrolyte, and separator. They are also equipped with safety devices, such as current interrupt device and top vent (Xu et al., 2021), and include electrolyte additives, such as flame retardant and/or stabilizers (Xing et al., 2022), to enhance the performance and the safety of the LIBs. Both the cathode and the anode are composed of two layers of active material deposited on the opposite faces of a metal foil acting as a current collector (made of aluminium (Al) for cathode and copper (Cu) for anode). Generally, the cathode is composed of mixed oxides of transition metals, such as lithium iron phosphate ($LiFePO_4$, LFP), lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$, NCM), lithium nickel cobalt aluminium oxide ($LiNiCoAlO_2$, NCA), or lithium cobalt oxide ($LiCoO_2$, LCO), deposited on the Al current collector while at the anode the active layer material, such as graphite (C) or lithium titanate oxide (Li_2TiO_3 , LTO), is deposited on the copper current collector. The function of the separator is dual as it avoids direct contact between the electrodes, which would cause an internal short circuit, allowing the migration of Li-ion from the anode to the cathode and vice versa during the use and charging phases. It is usually made of polymeric material, such as polyethylene (PE) and polypropylene (PP). Finally, the electrolyte is generally given

by various organic carbonates, such as ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and propylene carbonate (PC), in which a lithium salt is dissolved, such as lithium hexafluorophosphate (LiPF₆) or tetrafluoroborate (LiBF₄) (Hess et al., 2015). The electrolyte is an essential element, due to the significant impact on the electrochemical performance, but even a critical element, due to the presence of oxygen and trace of water, and its flammability as demonstrated by the flash-point close to room temperature for the main carbonates (i.e., 18 °C for DMC and 25 °C for DEC and EMC) (Hess et al., 2015). To enhance the performance and the safety of the device some additives are added to electrolyte reducing the flammability and the reactivity of these carbonates, while others as overcharge protection additives (Ming et al., 2019). The added flame-retardant compounds are usually phosphorus-containing organic compounds, such as (ethoxy)pentafluoro-cyclo-triphosphazene (PFPN). These additives suppress the flammability of the electrolyte by a physical char-forming process and a chemical reaction between the free radicals (Xing et al., 2022). The overcharge protection additives decompose on the cathode layer creating a very thin films that act as protection when the Li-ion cell is overcharging due to the electrochemically reversibility of compounds, such as 2,5-di-tertbutyl-1,4-dimethoxybenzene (DDB) (Xing et al., 2022).

However, there is a gap between the information reported in the safety data sheets (SDSs) of Li-ion cells and the internal chemical composition. In fact, in many available SDSs the quantities of internal components are expressed as a percentage, and some components are not well identified. The most common lack concerns the electrolyte, which is defined as a mixture of organic carbonates without specifying the solvents used in the mixture and their composition, or any other additives. In fact, in addition to improve the performance, safety issues must also be considered, such as flammability and/or the risk to human health and the environment when these substances are emitted from the LIB because the thermal runaway is triggered.

In this framework, this work aims to define a procedure to determine and quantify the internal components of Li-ion cells to fill the gap between the SDS information and the real internal composition of cells. To this aim three commercial Li-ion cells are considered with different composition of anode and cathode (i.e., C/NCA, LTO/NCA, and C/LFP). To analyse the internal components of the cell is necessary to disassembly it. Due to the flammability of the electrolyte, the cells were disassembled in an inert environment, such as a glovebox filled with argon. After separation, the electrodes have been analysed by Inductively Coupled Plasma coupled with the Optical Emission Spectrometer (ICP-OES), the electrolyte was extracted and analysed by Gas Chromatography coupled with Flame Ionization Detector (GC-FID) and Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry (SPME-GC-MS), while the separator was analysed by Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FT-IR) and Differential Scanning Calorimetry (DSC). The knowledge of the compounds and their compositions present inside the Li-ion cells is fundamental both to understand the reactions that occurred inside the cell leading to thermal runaway and to evaluate the risk to human health and the environment.

2. Materials and Methods

2.1 Materials

Three Li-ion cylindrical cells were considered, as reported in Table 1. Usually, the LIBs are named according to the cathode material (i.e., NCA, LFP) except for LTO which is referred to the anode material. For sake of clarity, in the following the id-code of the cells indicates both anode and cathode materials, i.e., the id-code C/NCA indicates a cell with graphite as anode and NCA as cathode. The cells were charged to the 50 % SoC respectively, after the solid electrolyte interphase (SEI) was formed through charge-discharge cycles.

Table 1: Cylindrical Li-ion cells and relative technical specification according to the SDS.

Chemical composition	Id-code	Technical specification
Anode: graphite (C) Cathode: Lithium nickel cobalt aluminium oxide (NCA)	C/NCA	Rated capacity: 3200 mAh Nominal voltage: 3.6 V
Anode: Lithium titanium oxide (LTO) Cathode: Lithium nickel cobalt aluminium oxide (NCA)	LTO/NCA	Rated capacity: 1300 mAh Nominal voltage: 2.4 V
Anode: graphite (C) Cathode: Lithium iron phosphate (LFP)	C/LFP	Rated capacity: 1300 mAh Nominal voltage: 3.2 V

2.2 Methods

2.2.1 Disassembly of the Li-ion cells

The Li-ion cells were carefully disassembled in a glove box filled with argon (O₂ and H₂O ≤ 0.1 ppm) with the use of an electric Dremel®, as shown in Figure 1. The disassembly operations were carried out in an inert atmosphere to avoid the risk of cell ignition, given the high reactivity of the electrolyte with air. At the end of the

disassembly operation, the internal roll was closed in a 50 mL test tube, to avoid the degradation of the materials, then centrifuged to extract the electrolyte and then unrolled to obtain the individual anode, cathode and separator foils.



Figure 1: Disassembly steps: (a) external case incision; (b) outer case incision; (c) electrodes separation.

2.2.2 Electrode characterization

The separated electrode foils were analysed by ICP-OES. This technique is applied to quantify the elemental composition of materials, with exceptions for some light elements or halogens. A mineralization step is performed involving dissolution in aqua regia (3:1 v/v HCl:HNO₃). Electrodes were previously homogenized using a laboratory agate mortar to obtain a fine powder. 0.150 g were weighed and were then placed in a muffle for 8 h at 530 °C. Then, 10 mL of reverse aqua regia (3:1 v/v HNO₃:HCl) were added to each sample. The digestion was performed at room temperature for 3 h shaking the sample. At the end of digestion, the samples were filtered, using quantitative filter paper, ashless, Grade 42, porosity 2.5 µm (Whatman™), into a flask and diluted with ultrapure water up to a final volume of 100 mL. Other dilutions, according to the sample, have been carried out.

2.2.3 Electrolyte characterization

The electrolyte was extracted from the cylindrical cells through centrifugation. The entire roll has been centrifuged for 30 min at 4200 rpm with a CL10 Centrifuge, ThermoScientific (Horsthemke et al., 2017). The roll was then removed and 50 µL of the electrolyte were transferred to a 1.5 mL vial and diluted with 950 µL of dichloromethane (DCM) for the GC-FID and SPME-GC-MS analysis. GC-FID analysis was performed with a GC-FID (Perkin Elmer) equipped with a StabilWax-DA - Restek column (30 m x 0.25 mm i.d. x 0.25 µm). Helium was used as carrier gas with a flow rate of 1 mL/min. The injector was held at 200 °C and 1.0 µL of sample was injected with a split ratio of 70:1, with the following temperature programme: from 40 °C to 100 °C with a heating rate of 5 °C/min, at 100 °C for 2.5 min and then up to 200 °C (10 min) with a heating rate of 30 °C/min. The detector was set to a temperature of 270 °C (Horsthemke et al. 2017). SPME was performed by means of a polyacrylate fiber (Supelco), previously conditioned for 30 min at 250°C. The vial was stirred for 5 min inside the switched-off oven, then, still under constant stirring, the fiber was exposed for 1 min in the head space of the vial. The fiber was desorbed inside the injector for 2 min with a split ratio of 1:25. The analyses were performed by a GC-MS (Agilent Technologies) connected to a Flex autosampler and a HP-5MS-Agilent Technologies, Inc. column (30 m x 0.25 mm i.d. x 0.25 µm). Helium was used as the carrier gas with a flow rate of 1.6 mL/min and a purge flow of 3 mL/min with the following programmed temperature: from 50 °C (2.5 min) up to 300 °C with a heating rate of 15 °C/min and maintained for 5 min. The MS works in EI mode with the ion source at 230 °C, interface at 280 °C and filament voltage at 70 eV. The mass spectra were acquired in scan mode, in the range 40-350 *m/z*. Mass spectra were compared with mass spectra available in the NIST library.

2.2.4 Separator characterization

Before characterisation analyses, the separator was washed with DCM to remove any residual electrolyte and/or additives. 5 g of the separator was immersed twice in 5 mL of fresh DCM, and finally the separator was dried to volatilise the residual extractants. The separator was analysed by ATR-FT-IR, using the Perkin Elmer Spectrum 3™ FT-IR Spectrometer, to identify the polymeric composition. Spectra were acquired using the following parameters: 4 cm⁻¹ as resolution, spectral range between 4000 and 650 cm⁻¹; 8 scans per spectrum and with triglycine sulphate (TGS) as detector. Spectra were identified by comparison with spectra available in the Perkin Elmer library. Then, the membrane was analysed by DSC to evaluate the melting temperature and enthalpy (ΔH) of the material. DSC analyses were performed on 3.0 mg of separator placed inside the aluminium capsule. DSC measurements were performed using a Perkin Elmer DSC instrument (model 8500) in nitrogen flow (40 mL/min) at 5 °C/min heating rate in the temperature range 25-200 °C. Experimental data were analysed by Pyris software (PerkinElmer).

3. Results

The inner roll of the cell, after centrifugation to extract the electrolyte, was unrolled to obtain the individual sheets of anode, cathode, and separator. The weight of the single components was measured and the weight percentage (% w/w), was calculated to be compared to the one reported in the SDS. In Table 2 is reported the weight of each component (g), the calculated percentage (% w/w), and the composition (%) from the SDSs.

Table 2: Internal components weight, percentage and SDS specification for C/NCA, LTO/NCA, and C/LFP.

	C/NCA			LTO/NCA			C/LFP		
	Weight (g)	Composition (%w/w)		Weight (g)	Composition (%w/w)		Weight (g)	Composition (%w/w)	
		Calculated	SDS		Calculated	SDS		Calculated	SDS
Anode and Cu foil	13.3551	41.5	31	14.3258	47.8	n.a.	11.4546	41.2	35
Cathode and Al foil	17.4816	54.5	54	13.2016	44.0	n.a.	14.1625	51.0	45
Separator foil	1.3198	4.1	3	2.3796	7.9	n.a.	2.1098	7.6	n.a.
Electrolyte	0.0614	0.19	12	0.0836	0.28	n.a.	0.0427	0.15	10
External case	8.3795	-	n.a.	5.6879	-	n.a.	5.1458	-	n.a.
Sum of components	40.5974	-	-	35.6785	-	-	32.9154	-	-
Whole cell	45.7384	-	-	40.2677	-	-	35.5858	-	-

n.a.: not available in the SDS.

There is a difference between the weight of the whole cell (Table 2) and the weight obtained by adding the individual components (Sum of components in Table 2), which is 5.1410 g for C/NCA, 4.5892 g for LTO/NCA, and 2.6704 for C/LFP. This difference appears to be due to the electrolyte, for which the calculated composition is lower than that reported in the SDS; in fact, both the electrodes and the separator remain impregnated with electrolyte after the cell is disassembled.

3.1 Electrode characterization

The element of the electrodes were identified by ICP-OES analysis. The quantities expressed in g of each electrode of C/NCA, LTO/NCA, and C/LFP cells are reported in Table 3.

Table 3: Elements (g) in the electrodes of C/NCA, LTO/NCA, and C/LFP by ICP-OES.

Electrode	Al (g)	Co (g)	Cu (g)	Fe (g)	Li (g)	Mn (g)	Ni (g)	P (g)	Ti (g)
C/NCA Anode	n.d.	n.d.	5.53	n.d.	0.21	n.d.	n.d.	n.d.	n.d.
C/NCA Cathode	4.73	1.58	n.d.	n.d.	0.30	< LOD	4.73	n.d.	n.d.
LTO/NCA Anode	n.d.	n.d.	3.22	n.d.	3.63	n.d.	n.d.	n.d.	4.77
LTO/NCA Cathode	5.33	1.37	n.d.	n.d.	0.28	0.05	5.61	n.d.	n.d.
C/LFP Anode	n.d.	n.d.	8.47	n.d.	0.25	n.d.	n.d.	n.d.	n.d.
C/LFP Cathode	4.27	n.d.	n.d.	3.04	0.09	n.d.	n.d.	0.44	n.d.

n.d.: not detected; LOD: limit of detection.

The analyses confirm the chemical composition expected, as reported in Table 1. Specifically, the chemical compositions found are: $(\text{Li}_{0.99}\text{Ni}_{0.71}\text{Co}_{0.15}\text{Al}_{0.15})\text{O}_2$ for NCA, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for LTO, and LiFePO_4 for LFP.

The co-presence of Li both in anode and cathode material is due to the state of charge of the cell (SoC=50 %), with a part of the Li intercalated in the anode material, and a part in the cathode material (Mao et al., 2019). About the cathode, where the Mn is present the amount obtained is very low, as for LTO/NCA cathode, or under the LOD of the instrument.

3.2 Electrolyte characterization

The electrolyte has been analysed to quantify both the organic carbonates (by GC-FID) and eventual additives compounds (by SPME-GC-MS). The electrolyte of the three cells was found to be composed by a mixture of DMC:DEC:EC in a different ratio. The predominant carbonate in C/NCA cell is DMC (DMC:DEC:EC ratio 2:1:1), in C/LFP cell is DEC (DMC:DEC:EC ratio 1.5:2:1), while in LTO/NCA cell DEC and EC are in the same ratio (DMC:DEC:EC ratio 1:1.5:1.5). The ratio is calculated considering only the organic carbonates in the electrolyte, but the SPME-GC-MS analysis revealed three additives: urea, N,N-dimethyl, dimethyl diglycol carbonate, and tetrahydrofuran. The composition of the three electrolytes is shown in Figure 2.

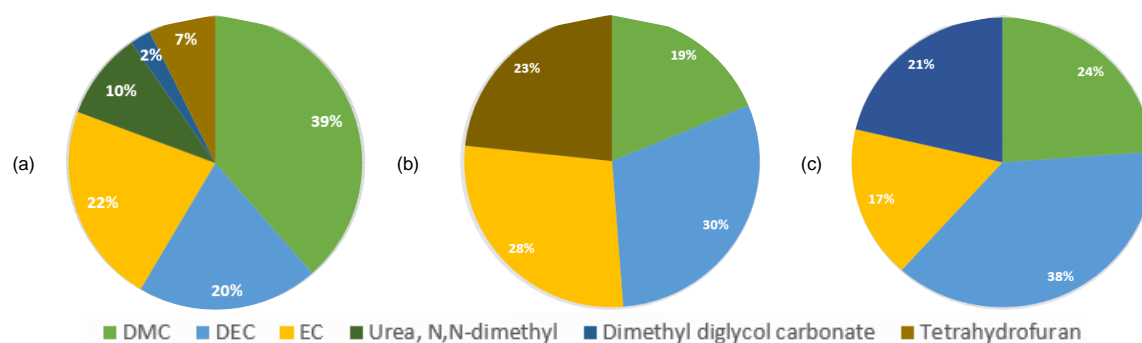


Figure 2: Electrolyte composition (% w/w) for each cell: (a) C/NCA; (b) LTO/NCA; (c) C/LFP.

From Figure 2 it is possible to observe that most of the electrolyte is given by the organic carbonates (in the range 77 and 81 %w/w), while additives have a percentage between 19 and 21 %w/w. These additives were probably added to increase the safety of the internal components enhancing the performance of the device, but they are not reported in the SDSs. Generally urea additives, such as urea, N,N-dimethyl, stabilize the Li-ion electrodes increasing the electrochemical performance of the cells (Kim et al., 2020). The dimethyl diglycol carbonate is added to the electrolyte to obtain a higher conductivity and a higher lithium cycling efficiency. The tetrahydrofuran is added to the electrolyte (La Monaca et al., 2018) to decrease the electrolyte decomposition stabilizing the organic SEI constituents (Paul-Orecchio et al., 2022). The SDS of these chemicals reveals, as reported in Table 4, that some of the additives raise safety concerns. The boiling point of tetrahydrofuran is 65 °C, which might lead to evaporation and an increase in internal pressure of the cell during an abuse. Due to the compounds' flammability, according to the hazard statements (H225: highly flammable liquid and vapor) and health hazards (H302: harmful if swallowed, H319: causes serious eye irritation, H335: may cause respiratory irritation), the release of it may have an impact on the flammability and toxicity of the electrolyte.

Table 4: Boiling temperature (°C), hazard pictogram, and hazard statements of the Li-ion cells additives.

Additive Compounds	T _{boiling} (°C)	Hazard pictogram (GHS)	Hazard statements (H)
Dimethyl diglycol carbonate	n.a.	GHS07	H315; H319; H335
Tetrahydrofuran	65	GHS02; GHS07; GHS08	H225; H302; H319; H335; H336; H351
Urea, N,N-dimethyl	268 - 270		H303

n.a.: not available.

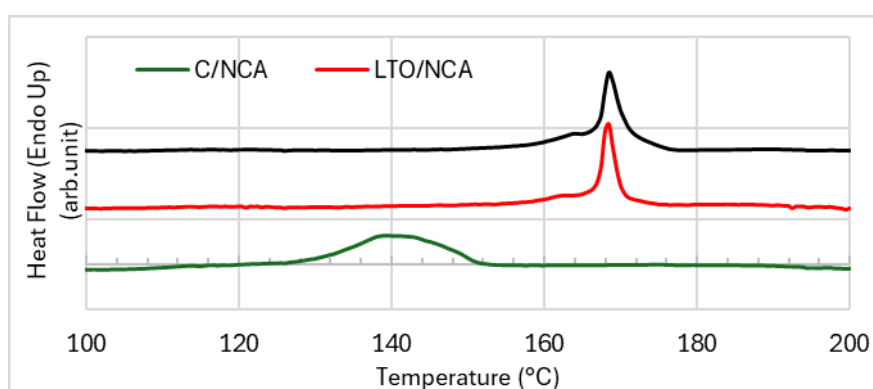


Figure 3: Thermograms of the separator for: (green line) C/NCA; (red line) LTO/NCA; (black line) C/LFP.

3.3 Separator characterization

The separator foils of the three cells are analysed both by ATR-FT-IR and by DSC, as shown in Figure 3. The ATR-FT-IR analysis identified the LTO/NCA and C/LFP separators as PP, while in the case of C/NCA it was identified as high density PE (HDPE) (Signoret et al., 2019). The results are also confirmed by the thermograms, Figure 3, where three endothermic peaks are observed at 140 ± 1 °C with a ΔH of 81 ± 27 J/g (C/NCA). The temperature is close to the melting temperatures of 135 °C for HDPE. The other two thermograms

show an endothermic peak at 168 ± 0.1 °C with a ΔH of 41 ± 5 J/g (LTO/NCA) and at 168 ± 0.4 °C with a ΔH of 27 ± 1 J/g (C/LFP), both close to the melting temperature of PP, around 165 °C.

4. Conclusions

The characterization of three cylindrical Li-ion cells, C/NCA, LTO/NCA, and C/LFP, available on the market was performed to fill the gap between the SDS information and the real chemical composition of the different components, i.e., electrodes, electrolyte and separator in the cell. The ICP-OES analysis confirms the metal composition of the electrodes, while the chemical composition of the separators and their thermal stability have been evaluated by DSC analysis. The most interesting finding regards the electrolyte: in fact, combining the GC-FID and SPME-GC-MS results, it was possible to identify the total composition of the electrolyte, not just the organic carbonate with the relative ratio, i.e., DMC, DEC, and EC, but even the additives, like tetrahydrofuran, added to the electrolyte to enhance the performance of the cells and in some cases to ensure their safety. The analytical methods proposed can be used for other types of LIBs. In particular, it is important to identify electrolyte chemical composition and the additives because, in case of release, they might have consequences on human health and environment.

Acknowledgments

This study was carried out within the SAFERA 2022 project "Safety evaluation of nanomaterials in Novel EES materials and LIBs (Nano-SaNE)" and MOST – Sustainable Mobility Center and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4 – D.D. 1033 17/06/2022, CN00000023). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered responsible for them.

References

- Hess S., Wohlfahrt-Mehrens M., Wachtler M., 2015, Flammability of Li-Ion Battery Electrolytes: Flash Point and Self-Extinguishing Time Measurements, *J. Electrochem. Soc.*, 162, 2, A3084–A3097.
- Horsthemke F., Friesen A., Mönninghoff X., Stenxel Y.P., Grütze M., Andersson J.T., Winter M., Nowak S., 2017, Fast screening method to characterize lithium ion battery electrolytes by means of solid phase microextraction–gas chromatography–mass spectrometry," *RSC Adv.*, 7, 74, 46989–46998.
- Kim H.-S., Verma R., Kim J., Park C.-J., 2020, Effect of Urea as Electrolyte Additive for Stabilization of Lithium Metal Electrodes, *ACS Sustainable Chem. Eng.*, 8, 30, 11123–11132.
- La Monaca A., De Giorgio F., Soavi F., Arbizzani C., Tarquini G., Di Carli M., Prosini P.P., 2018, 1,3-Dioxolane: A Strategy to Improve Electrode Interfaces in Lithium Ion and Lithium-Sulfur Batteries, *ChemElectroChem*, 5, 9, 1272–1278.
- Mao N., Wang Z.-R., Chung Y.-H., Shu C.-M., 2019, Overcharge cycling effect on the thermal behavior, structure, and material of lithium-ion batteries, *Applied Thermal Engineering*, 163, 114147.
- Ming J., Cao Z., Wu Y., Wahyudi W., Wang W., Guo X., Cavallo L., Hwang J.-Y., Shamim A., Li L.-J., Sun Y.-K., Alshareef H.N., 2019, New Insight on the Role of Electrolyte Additives in Rechargeable Lithium Ion Batteries, *ACS Energy Lett.*, 4, 11, 2613–2622.
- Paul-Orecchio A. G., Weeks J. A., Dolocan A., Mullins C. B., 2022, High-Stability Lithium Metal Batteries Enabled by a Tetrahydrofuran-Based Electrolyte Mixture, *ACS Appl. Energy Mater.*, 5, 8, 9437–9446.
- Qiu Y., Jiang F., 2022, A review on passive and active strategies of enhancing the safety of lithium-ion batteries, *International Journal of Heat and Mass Transfer*, 184, 122288.
- Signoret C., Caro-Bretelle A.-S., Lopez-Cuesta J.-M., Ienny P., Perrin D., 2019, MIR spectral characterization of plastic to enable discrimination in an industrial recycling context: II. Specific case of polyolefins, *Waste Management*, 98, 160-172.
- Xing J., Bliznakov S., Bonville L., Oljaca M., Maric R., 2022, A Review of Nonaqueous Electrolytes, Binders, and Separators for Lithium-Ion Batteries *Electrochem. Energy Rev.*, 5, 4, 14.
- Xu B., Kong L., Wen G., Pecht M. G., 2021, Protection Devices in Commercial 18650 Lithium-Ion Batteries, *IEEE Access*, 9, 66687–66695.
- Zhang R., Xia B., Li B., Cao L., Lai Y., Zheng W., Wang H., Wang W., 2018. State of the Art of Lithium-Ion Battery SOC Estimation for Electrical Vehicles, *Energies*, 11, 7, 1820.