Report on the state of the art for N-Methyl-2-pyrrolidone in the production of lithium-ion battery cells

Executive Summary

This report describes the current state of the art for lithium-ion battery cell production and the need to use N-Methyl-2-pyrrolidone (NMP) as a solvent in cathode manufacturing.

First, the physical and chemical properties as well as the environmental and health risks of NMP are presented. In order to assess the possibility of elimination or substitution, the current technological status of cathode production is described with focus on the use of NMP as a solvent. For the evaluation of an elimination of NMP and thus a solvent-free cathode production, the dry coating process and the production of the All-Solid-State batteries are explained. Both technologies show promising results due to stable coatings with good electrochemical properties. However, the coatings have only been produced on a laboratory scale so far. The implementation of these technologies on an industrial scale is currently not possible due to process sequences and process times. The substitution of NMP in industrial scale by water or other organic solvents is currently not feasible, either. There are three main problems when using a water-based mixing process: Agglomeration of the NMC particles, decreased wetting behaviour of the slurry on the aluminium foil and limited stability of NMC due to the formation of LiOH groups on the NMC particle surface. As a result, cathode production on an industrial scale must be performed according to the current state of technology with NMP as the solvent, as there are currently no alternatives. The report demonstrates that remaining health and environmental risks can be managed by certain precautions. Taking the current status of cell chemistry technologies and production technologies into account, it is estimated that a technology change in industrial battery cell production could take place within the next 5-10 years.[1]

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[1] Assessment of the Chair of Production Engineering of E-Mobility Components, RWTH Aachen University, 2019.

Contents

1 Characteristics of NMP

1.1 Physical and Chemical characteristics

N-Methyl-2-pyrrolidone is a colourless hygroscopic, air and light sensitive organic liquid with a mild amine smell. It is soluble in water as well as in most organic solvents including alcohols, ethers, aromatics, and chlorinated hydrocarbons. It has a relatively low vapour pressure of 0.7 mbar at 25 °C and therefore evaporates slowly.[2]

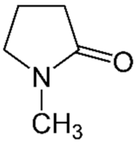

Figure 1: Structural formula of N-Methyl-2-pyrrolidone.

NMP is a very weak base, a 10% aqueous solution shows a pH value of 7.7 to 8.0, the compound is chemically very stable. The lactam ring can only be opened with strong acids and bases, resulting in 4-*N*-Methylaminobutyric acid. NMP is only stable to oxygen to a limited extent, with oxidation starting at the 5-position and *N*-Methylsuccinimide being formed via various intermediate stages. NMP forms flammable vapour-air mixtures above the flash point of 91 °C. The explosion range lies between 1.3 vol.% as the lower explosion limit and 9.5 vol.% (393 $g \cdot m^3$) as upper explosion limit. A correlation of the lower explosion limit with the vapour pressure function results in a lower explosion point of 79 °C. The limiting oxygen concentration at 200 °C is 8.1 vol.%. The limiting gap width was determined to be 0.93 mm. This results in an assignment to explosion group IIA. The ignition temperature is 265 °C. The substances therefore falls into temperature class T3. NMP decomposes at a temperature above 300 °C, producing carbon monoxide, carbon dioxide, nitrous gases and hydrogen cyanide. The conductivity is at $2 \cdot 10^{-6}\ S \cdot m^{-1}$.[3] An overview of the physical and chemical properties is given in Table 1.

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[2] O. Ajayi, E. Harriman, N-Methyl Pyrrolidone: Chemical Profile, Technical Report No. 36, 1996, The Massachusetts Toxics Use Reduction Institute, University of Massachusetts Lowell

[3] Technical Data Sheet, NMP, Hefei TNJ Chemical Industry Co., Ltd, 2019.

Table 1: Overview of physical and chemical properties of N-Methyl-2-pyrrolidone (99%).[4]

Name	*N*-Methyl-2-pyrrolidone 1-Methylpyrrolidin-2-one *N*-Methylpyrrolidone *N*-Methylpyrrolidinone Pharmasolve
CAS number	872-50-4
Molecular formula	C_5H_9NO
Molecular weight	$99.133\ g\cdot mol^{-1}$
Density	$1.0300\ g\cdot cm^{-3}$ at 25 °C
Viscosity	1.67 mPa at 20 °C
Melting point	-24 °C
Boiling point	202 °C
Flash point	91 °C
Autoignition temperature	346 °C
Explosion limits	1.3 vol.% (lower) 9.5 vol.% (upper)
Vapour pressure	0.7 mbar
Vapour density	3.4 (Reference: Air = 1.0)
Surface tension	$40.7\ mN\cdot m^{-1}$
Solubility in	Water ($1000\ g\cdot cm^{-3}$), ethanol, acetone, diethylether, ethyl acetate, chloroform, benzene
Vapour pressure	0.7 mbar at 25 °C
pH ($100\ g\cdot L^{-1)}$	7.7-8.0

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[4] Safety Data Sheet, ThermoFisher Scientific, 2019

1.2 Environmental and health impacts

The following chapter lists the hazard information for NMP in tabular form.

Table 2: Hazard Statements of N-Methyl-2-pyrrolidone (99%).[5]

Pictograms	 Irritant  Health hazard
Skin Corrosion/irritation	Category 2 H315 – Causes skin irritation
Serious Eye Damage/Eye Irritation	Category 2 H319 – Causes serious eye irritation
Reproductive Toxicity	Category 1B H360D – May damage the unborn child
Specific target organ toxicity	Category 3 H335 – May cause respiratory irritation
Toxicity	Threshold Limit Value estimated at 100 ppm[6]
Special hazards	Combustible material. Containers may explode when heated. Keep product and empty container away from heat and sources of ignition.

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[5] Safety Data Sheet, ThermoFisher Scientific, 2019.

[6] O. Ajayi, E. Harriman, N-Methyl Pyrrolidone: Chemical Profile, Technical Report No. 36, 1996, The Massachusetts Toxics Use Reduction Institute, University of Massachusetts Lowell (value for 8 working hours).

Table 3: Toxicological parameters of N-Methyl-2-pyrrolidone (99%).[7]

Toxicity	Threshold Limit Value estimated at 100 ppm[8]
LD 50 Oral	3914 mg·kg^{-1} (Rat)
LD 50 Dermal	8 g·kg^{-1} (Rabbit)
LC 50 Inhalation	>5.1 mg·L^{-1} (Rat) 4hr
Fresh water PNEC[9]	0.25 mg·L^{-1}
Fresh water sediment PNEC	0.805 mg·kg^{-1}
Marine water PNEC	0.025 mg·L^{-1}
Marine water sediment PNEC	0.0805 mg·kg^{-1}
Food chain PNEC	0.00167 g·kg^{-1}
Microorganisms in sewage	10 mg·L^{-1}
Soil (Agriculture)	0.138 mg·kg^{-1}
Hazardous Combustion products	Carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), peroxides

Table 4: Precautionary Statements of N-Methyl-2-pyrrolidone (99%).[10]

Skin Corrosion/irritation	P302 + P352 – Wash with plenty of soap and water
Serious Eye Damage/Eye Irritation	P337 + P313 – Get medical advice / attention
Reproductive Toxicity	P312 – Call a Poison Centre or doctor / physician if you feel unwell
Specific target organ toxicity	P304 + P340 – Remove to fresh air and keep at rest in a position comfortable for breathing
Personal precautions, protective equipment and emergency procedure	Use personnel protective equipment. Ensure adequate ventilation. Keep people away from and upwind of Spill/leak. Evacuate personnel to safe areas. Remove all sources

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[7] Safety Data Sheet, ThermoFisher Scientific, 2019.

[8] O. Ajayi, E. Harriman, N-Methyl Pyrrolidone: Chemical Profile, Technical Report No. 36, 1996, The Massachusetts Toxics Use Reduction Institute, University of Massachusetts Lowell (value for 8 working hours).

[9] Predicted No Effect Concentration.

[10] Safety Data Sheet, ThermoFisher Scientific, 2019.

other	P280 – Wear protective gloves / protective clothing / eye protection / face protection P332 + P313 – If skin irritation occurs: Get medical advice / attention

Studies in rats on the toxic effect of NMP show a negative influence on the foetus in pregnancy and suggest mutagenic effect.[11],[12] In summary, it must be assumed that NMP is mutagenic and causes skin, eye and respiratory irritations.

Nevertheless, there will be no environmental impact from NMP as long as the quantities of NMP released are kept below the levels shown in Table 5.

Table 5: Environment impact of N-Methyl-2-pyrrolidone (99%).[13]

	Threshold value	Environmental compartment	Exposure duration
PNEC[14]	5 mg·L^{-1}	water	Intermittent release
PNEC	0.25 mg·L^{-1}	Fresh water	Short term (one time)
PNEC	0.025 mg·L^{-1}	Seawater	Short term (one time)
PNEC	10 mg·L^{-1}	Sewage treatment plant (STP)	Short term (one time)
PNEC	1.09 mg·kg^{-1}	Fresh water sediment	Short term (one time)
PNEC	0.109 mg·kg^{-1}	Seawater sediment	Short term (one time)
PNEC	0.07 mg·kg^{-1}	Soil	Short term (one time)

Based on different studies, NMP has been classified as readily biodegradable under aerobic conditions, as under various conditions at least 95% of NMP was biodegraded within a maximum of 2 weeks.[15,16]

As the calculated bio-concentration factor of NMP is 0.16, only a minor potential for bioaccumulation is to be expected (cf. Table 6).

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[11] Hass et al., Developmental Toxicity of Inhaled N-Methylpyrrolidone in the Rat, Pharmacology & Toxicology, 76, 406-409, 1995.

[12] Saillenfait et al., Development toxicity of N-methyl-2-pyrrolidone administered orally to rats, Food and Chemical Toxicology, 40, 1705-1712, 2002.

[13] Safety Data Sheet, Roth, P052, 2019.

[14] Predicted No Effect Concentration.

[15] N-Methyl Pyrrolidone: Chemical Profil, Technical Report No. 36, University of Massachusetts Lowell, 1996.

[16] N-Methyl-2-Pyrrolidone, Concise International Chemical Assessment Document 35, World Health Organization, 2001.

Table 6: Rough estimation of bioconcentration factor values.[17]

BCF	
<1	Non-bioaccumulative
1-10	Weakly bioaccumulative
10-100	Moderately bioaccumulative
100-1000	bioaccumulative
1000-5000	Highly bioaccumulative
>5000	Very high bioaccumulative

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[17] www.bgbau.de, 2020.

2 Applications and advantages in LiB production

N-Methyl-2-pyrrolidone (NMP) is typically used in the manufacturing process of lithium-ion batteries as a solvent for cathode slurries to obtain a stable suspension. In a mixing process, the cathode active material and conductive additives, the binder (typically PVDF) and the solvent NMP are mixed together for producing the so-called slurry. $LiCoO_2$ (LCO), $LiMn_2O_4$ (LMO), LiFePO4 (LFP) and $LiNi_xMn_yCo_zO_2$ (NMC) are typical cathode materials that are used in the production of lithium-ion batteries.[18] First, the solids are premixed dry, then the solids are dispersed homogeneously in the solvent and agglomerates are dissolved. Depending on the slurry components, this process step can be carried out in different types of mixers with different mixing tools. To avoid air inclusions in the slurry, mixing is usually done under vacuum, which requires a closed system. The slurry is then transferred via a sealed pump system to the coating plant and is applied to the electrode carrier foil by a coating tool such as a slot die. The used composite structure of the active material, binders, and conductive additives coated on the current collector foil requires careful control of colloidal chemistry, adhesion, and solidification. The use of NMP requires a closed system for all process steps to prevent contamination of the environment with NMP. After the coating process, the NMP is totally removed from the cathode material during the subsequent drying process. With the help of suitable exhaust air systems, NMP can be collected and can be purified for reuse.

As NMP has the properties listed above, handling requires dedicated safety standards and contact with strong oxidizing agents, strong acids, strong bases, heat, flames, sparks hot surfaces and sources of ignition should be avoided. The flammable vapours of NMP require all processing equipment during the production of electrodes to be explosion proof, meaning all spark-producing electrical components need to be shielded against vapour concentrations.

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[18] Li et al. Cathode Manufacturing for Lithium-Ion Batteries, Handbook of Battery Materials, Wiley-VCH-Verlag, 2011.

3 Evaluation Approach

Because *N*-Methyl-2-pyrrolidone (NMP) has the described harmful properties, the long-term goal should be to eliminate or at least replace NMP with a less hazardous solvent in battery cell production. Therefore, chapter 3.1 investigates LIB production technologies that help to eliminate the usage of NMP. If elimination is not possible, a substitution of NMP by other solvents in LIB cell production is discussed in the following chapter. An extensive literature research was carried out to highlight the state-of-the-art research on solvents in LIB production. Finally, a remaining risk assessment will be conducted for processes using NMP as a solvent.

3.1 Elimination

Commercial Li-ion battery electrodes are manufactured by coating a metal foil (current collector) with a slurry as described in chapter 2 (Applications and advantages in LiB production). In order to assess whether NMP can be eliminated in the LIB production, solvent-free manufacturing technologies are considered. Studies using pulsed laser and sputtering[19] deposition have shown that dry particle deposition is possible in general, but these processes are not suitable for commercial applications due to prolonged manufacturing time.[20,21,22,23] A solvent-free dry spray manufacturing process was also carried out in a study on a laboratory scale with promising results, which, however, must be further developed and evaluated for industrial production.[24] From similar technology development activities, one can say that this will take at least 5-10 years until this technology is ready for mass production.

In addition to that, the usage of environmentally hazardous solvents can be avoided by a complete technological change, for example the use of All-Solid-

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[19] Sputtering: Sputter deposition is a physical vapor deposition method of thin film deposition. This involves ejecting material from a target that is a source onto a substrate

[20] Yan et al., Li-rich Thin Film Cathode Prepared by Pulsed Laser Deposition, Sci. Rep., 3, 3332, 2013.

[21] Koike et al., Preparation and performance of higly porous layered LiCoO2 films for lithium batteries, J. Power Sources, 174, 976-980, 2007.

[22] Bagetto et al., Fabrication and characterization of Li-Mn-Ni-O sputtered thin film high voltage cathodes for Li-ion batteries, J. Power Sources, 211, 108-118, 2012.

[23] Chiu, Lithium cobalt oxide thin films deposited at low temperature by ionized magnetron sputtering, Thin Solid Films, 515, 4614, 2007.

[24] Ludwig et al., Understanding Interfacial-Energy-Driven Dry Powder Mixing for Solvent-Free Additive Manufacturing of Li-ion Battery Electrodes, Adv. Mater. Interfaces, 2017 (1700570).

State batteries. For the production of the cathode in All-Solid-State batteries theoretically different materials like LFP, NMC and LCO can be used. In practice only LCO as cathode material in combination with LLZO as electrolyte shows sufficient stability and performance. These two materials are converted separately into a homogenous melt by means of twin screw extruder and are then calendered to a composite. By using this method, no solvent is required in the production of the cathode material. The cathode/electrolyte composite and the anode, usually metallic lithium, are pressed together by rolls. Alternatively, the All-Solid-State battery can be combined by high-frequency sputtering of the cathode and electrolyte powder and subsequent sintering. Both processes do not require a solvent, consequently NMP can be eliminated with the application of this technology. Nevertheless, challenges in material compatibility and industrial manufacturability – as sputter deposition methods usually show very low tact times – inhibit the entry into industrial production for All-Solid-State batteries.[25]

In our estimation, the developments of the technologies listed here for the elimination of NMP as a solvent in cathode production require a further 5-10 years before they can be carried out on an industrial scale.[26]

3.2 Substitution

For a substitution of NMP as solvent of the active material for the cathode, the properties of the solvents must be compared with each other. Due to the low costs, environmental compatibility as well as non-flammability, the use of water as a solvent in cathode production mostly with regard to lithium ion phosphate (LFP) as active material is often discussed.[27,28] This is due to the much higher stability of LFP to water compared to other cathode materials such as NMC. The lower specific capacity of LFP (165 $mAh \cdot g^{-1}$) in comparison to NMC (NMC 111: 180 $mAh\ g^{-1}$; NMC 811: >200 $mAh \cdot g^{-1}$) as well as the lower average voltage (LFP: 3.4 V; NMC: 3.7 V) and high quality demands from automotive

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[25] Heimes et al., Production of All-Solid-State battery cells, Printed by PEM of RWTH Aachen and VDMA, 2018.

[26] Assessment of the Chair of Production Engineering of E-Mobility Components, RWTH Aachen University, 2019.

[27] Li et al., Superior Performance of $LiFePO_4$ Aqueous Dispersions via Corona Treatment and Surface Energy Optimization, J. Electrochem. Soc., 159 (8), 2012.

[28] Daniel, Lithium Ion Batteries and Their Manufacturing Challenges, The National Academies of Science, Engineering, and Medicine, 2015.

industry have limited its adoption into the electric vehicle market.[29,30,31] Nevertheless, solutions for water-based cathode production methods are repeatedly discussed, which is why the challenges of water-based NMC coating are briefly explained in the following. Water is a polar solvent and has hydrophilic properties, whereas NMP is a non-polar organic solvent with hydrophobic properties. When water is used, the cathode active material tends to agglomerate. In addition, the surface wetting of the aluminium foil with the water-based slurry is significantly worse due to the higher surface tension of water (70 $mN \cdot m^{-1}$) compared to NMP(40 $mN \cdot m^{-1}$).[32] The poorer surface wetting leads to reduced adhesion of active material coating. This in turn leads to decreased battery performance and can even lead to battery failure if the active material coating becomes detached.

Laboratory-scale studies showed that the surface charge and thus the hydrophilicity of the active material particles can be influenced by modification with functional groups, for example by using phosphoric acid to apply a nanometre thick $LiPO_4$ coating[33]. This can prevent agglomeration formation but the modification, however, is costly and time-consuming. In addition, phosphoric acid as a corrosive chemical also poses a certain risk potential.[34] In the production of phosphoric acid, rock phosphate (apatite) is also reacted with another acid, such as sulphuric or hydrochloric acid. This process therefore also has a potential risk. Thus, the total amount of environmentally harmful chemicals used would not be minimized by substitution with water. The agglomeration of the active material NMC in water could most probably also be prevented by the addition of stabilizing agents. However, since this has been investigated on a laboratory scale and certainly not on an industrial scale, these are assumptions that need to be investigated in more detail.[35] Another aspect of using water as solvent to coat the cathode with NMC is the chemical stability of NMC to water. The Lithium-Oxygen species present in NMC (Li_2O, Li_2O_2) already react with water from the ambient air

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[29] Li et al., 30 Years of Lithium-Ion Batteries, Adv. Mater., 30, 2018 (1800561).

[30] Nitta et al., Li-ion battery materials: present and future, Mater. Today, 18, 2015.

[31] Thackeray et al., The Quest for Manganese-Rich Electrodes for Lithium Batteries: Strategic Design and Electrochemical Behaviour, Energy & Fuels, 2, 2019.

[32] Li et al. Cathode Manufacturing for Lithium-Ion Batteries, Handbook of Battery Materials, Wiley-VCH-Verlag, 2011.

[33] Jo et al., An effective method to reduce residual lithium compounds on Ni-rich $Li[Ni_{0.6}Co_{0.6}Mn_{0.2}]O_2$ active material using a phosphoric acid derived Li3PO4 nanolayer, Nano Research, 8(5), 1464-1479, 2014.

[34] Safety Data Sheet, Fisher Science, S25470B, 2020.

[35] Li et al., Superior Performance of LiFePO4 Aqueous Dispersions via Corona Treatment and Surface Energy Optimization, J. Electrochem. Soc., 159 (8), 2012.

to form LiOH on the particle surface. It is assumed that a water-based NMC coating will react with water in the same way. The formed LiOH layer causes large irreversible capacity decrease during the initial cycle. During the successive charge-discharge cycles, the water is released again, resulting in decomposition of the $LiPF_6$ electrolyte salt and formation of HF.[36] Furthermore, a recent study from 2019 confirmed the influence of contamination with water in particular on NMC 111 und NMC 811. Here, the properties of wet and dry NMC 111 and NMC 811 are compared, whereby a higher influence of the water by decreasing the electrochemical performance of NMC 811 can be determined.[37] This is supported by previous studies which found a higher water affinity for high-nickel cathodes.[38]
In spite of the studies on the limited water stability of NMC, there are a few studies on water-based cathode materials, e.g. about ultra-thick NMC 111 coatings. However, the approach described there was carried out exclusively on a laboratory scale with NMC 111 and tested on coin cells. Therefore, the technologies developed there have to be further evaluated for a transfer into industrial production and for larger cell designs.[39]
A further possibility of substituting NMP in LIB production is the usage of organic solvents with comparable physical and chemical properties.
The solvents dimethylacetamide (DMAc), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) listed in Table 7 were identified as possible substituents.

Table 7: Physical and chemical characteristics of identified organic solvents which could be used to substitute NMP.

Parameters	Solvents			
	NMP	DMAc	DMF	DMSO
Flammability	Moderate	Moderate	Highly	Moderate
Flash Point [°C]	93	63	57.7	89
Toxicity	Toxic	Less toxic than DMF	More toxic	Non-toxic
Vapour pressure [hPa; 20°C]	0.32	3.3	3.77	0.556

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[36] Hou et al., Surface/Inerfacial Structure and Chemistry of High-Energy Nickel-Rich Layered Oxide Cathodes: Advances and Perspectives, Small, 13, 2017 (1701802).
[37] Sicklinger et al., Ambient Storage Derived Surface Conatmination of NMC811 and NMC111: Performance Implications and Mitigation Strategies, J. Electrochem. Soc., 166 (12), 2019.
[38] You et al., Stable surface chemistry against ambient air of modified high-nickel cathodes for lithium-ion batteries, Angew. Chem. Int. Ed., 57, 6480, 2018.
[39] Ibing et al., Journal of Power Sources 423, 183-191, 2019.

Acute Permeability Constant $[g \cdot m^{-2}h^{-1}]$	171 (fast in skin penetration)	107 (slow in skin penetration)	98 (slower in skin penetration)	176 (faster in skin penetration)
Threshold Limit Values established	100 ppm	10 ppm	10 ppm	None established
Environmental Fate	Moderately bio-degradable	Half-life of less than one day in the air	Not readily biodegradable, half-life of one year or more	Biodegradable and environ-mentally safe

Since toxicity and environmental fate are one of the main criteria for selecting suitable substitutesfor NMP, only the use of DMSO can improve LIB production.
DMSO is chemically stable and has a high relative permittivity[40] of 46.7[41], high oxidation potential and high boiling temperature, why DMSO is discussed both as solvent in cathode production and as electrolyte in lithium-ion batteries.[42] However, DMSO in combination with NMC can form by-products, such as Li_2CO_3. Like LiOH, Li_2CO_3 act as an insulating layer to inhibit lithium ion conductivity and impairs the electrochemical properties, especially during long-term cycles.[43]
The results of a study in laboratory scale has shown a possible substitution of NMP by using DMSO. Nevertheless, the cathodes were only examined in small coin cells.[44] Publications about scale-up or larger cathode production with DMSO as solvent could not be found.
Studies on the substitution of NMP in other industrial applications, for example as solvent for cleaning polyurethane resin from parts and equipment in the production of urethane foam products, have shown that certain properties of the solvent are also required in this case. However, since these properties do not correspond to those of NMP in LIB production, the studies are not explained in detail here.[45]
Finally, it has to be mentioned that there are only few publications on reagents for the substitution of NMP as a solvent in cathode production, which obviously reflects the difficulty of substituting NMP.

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[40] Permittivity is a material property that affects the Coulomb force between two point charges in the material. Relative permittivity is the factor by which the electric field between the charges is decreased relative to vacuum.

[41] https://roempp.thieme.de/roempp4.0/do/data/RD-04-01767, 15.12.2019.

[42] Kim et al., Lithium-ion batteries: outlook on present, future, and hybridized technologies, J. Mater. Chem. A., 7, 2942-2964, 2019.

[43] Hou et al., Surface/Inerfacial Structure and Chemistry of High-Energy Nickel-Rich Layered Oxide Cathodes: Advances and Perspectives, Small, 13, 2017 (1701802).

[44] Bankole et.al., Environmental Compatible Dimethyl Sulfoxide: an Alternative to N-methylpyrrolidone for Electrochemical Performance of Recycled $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ in Lithium-Ion Battery, Russ J Electrochem, 2013, DOI: 10.1134/S1023193514030021

[45] Case Study: NMP Replacement Solution, JR Hess Company, 2016.

In order to eliminate or substitute NMP from cathode production in long term, UKBIC should track the technology development of lithium-ion battery production in the future and should check where new technologies can be integrated into the manufacturing environment.

3.3 Remaining Risk assessment

As explained in the previous chapters, it is not possible to eliminate or substitute NMP in lithium-ion battery production according to the current state of research and technology. Therefore, the following section explains the prevention of hazard minimisation and safety enhancement in the cathode production of lithium-ion batteries.

In order to avoid contamination with NMP and especially for the health protection of the workers, cathode production is carried out in a closed system. This means that the mixing process of the active material, NMP and additives should be performed in an air-tight vessel and the slurry should be transferred to the coating head using a sealed pump system. By equipping the cathode coaters with a solvent recovery system, the NMP can be removed directly from the plant and can be collected by condensation. For example, the use of a recirculation fan and the control of the supply air flow by dampers as well as a 3-stage condenser is a suitable extraction system for NMP. Small amounts of NMP can also be collected in a carbon filter where the air is cleaned to a residual of $<0{,}5\ \mathrm{g{\cdot}m^{-3}}$.The NMP is finally professionally transported and disposed of in a closed system.

The cathode production with NMP as solvent is performed successfully and safely at various established cell manufacturers (CATL, Custom Cells, etc.) in the described process. As cathode production uses NMP emission values below $10\ \mathrm{g{\cdot}h^{-1}}$, these hazard prevention methods are be considered sufficient.[46]

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[46] The Solvent Emissions Directive – For the Environmental Permitting (England and Wales) Reguslations 2010, Version 3.0.

4 Current regulations in Europe

Different regulations apply to Europe, which are listed below and briefly explained.

The **Directives 2010/75/EU of the European Parliament and the Council of 24 November 2010 on industrial emissions** contain the regulations for the approval of an installation. In *L334/18 (5)* it is said, that to ensure the prevention and control of pollution, each installation should operate only if it holds a permit or in case of certain installations and activities using organic solutions, only if it holds a permit or is registered. For this purpose, it was stipulated in *L334/19 (15)* that is it important to provide sufficient flexibility to competent authorities to set emission limit values that ensure that, under normal operating conditions, emissions do not exceed the emission levels associated with the best available techniques. To this end, the competent authority may set emission limits that differ from the emission levels associated with the best available techniques in terms of the values, periods of time and reference conditions applied, so long as it can be demonstrated, through the results of emission monitoring, that emissions have not exceeded the emission levels associated with the best available techniques. Compliance with the emission limit values that are set in permits results in emissions below those emission limit values. In addition, it is said in the section *L334/18 (16)* that in order to take into account certain specific circumstances where the application of emission levels associated with the best available techniques would lead to disproportionately high costs compared to the environmental benefits, competent authorities should be able to set emission limit values deviating from those levels. Such deviations should be based on an assessment taking into account well-defined criteria. The emission limit values set out in this Directive should not be exceeded. In any event, no significant pollution should be caused and a high level of protection of the environment taken as a whole should be achieved. If the installation contains the best available techniques in accordance with *L334/23 (10)* and the operator demonstrates to the competent authority that for an individual installation the emission limit value for fugitive emissions is not technically and economically feasible, the competent authority may allow emissions to exceed that emission limit value provided that significant risks to human health or the environment are not to be expected and that the operator demonstrates to the competent authority that the best available techniques are being used *(L334/44, Article 59).*

As described above, both the use of the best available technique an no substitutability of the NMP applies in this case, to that the emission limit values could be adjusted.

In addition, **EUROBAT** (Association of European Automotive and Industrial Battery Manufactures) has published a recommendation on the usage of NMP in the lithium-ion battery industry. In the key recommendations it is said that no alternatives are available today for the battery industry use. The advice given by **RAC/SEAC** in November to EU Commission to opt for restriction for NMP (reduced occupational limit) as the best risk management option, is perfectly suitable for the batteries manufacturing. Furthermore, the implementation harmonized OHS requirements has also taken place by already implemented the valid OEL-value for NMP of 40 $mg \cdot m^{-3}$ as derived by SCOEL as the appropriate protection measure for industrial use.

NMP was added to the **Federal Toxics Release Inventory (TRI)** and **Toxics Use Reduction Act (TURA)** list of reportable chemicals on November 30, 1994 for the 1995 reporting year. An Environmental Protection Agency NMP-specific assessment began in response to information indicating that exposure to NMP could present a significant risk of reproductive and developmental harm to humans. The Final Assessment concludes that such a reproductive and developmental risk does exist. **EU-Commission Directive 2006/15/EC** of 7 February 2006 establishing a second list of indicative occupational exposure limit value in implementation of Council Directive 98/24/EC and amending Directives 91/322/EEC and 2000/39/EC on the protection of the health and safety of workers from the risks related to chemical agents at work.[47]

The **UK-EH40** containing the workplace exposure limits (WELs) for use with the Control of Substances Hazardous to Health Regulations (COSHH) 2002 (as amended) and were updated by September 2006 official press release and October 2007 Supplement.[48] Furthermore **IRE-2010 Code of Practice for the Safety, Health and Welfare at Work** (Chemical Agents) published regulations in 2001 by the Health and Safety Authority.[49] The data of the mentioned regulations are shown in Table 8.

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[47] Safety Data Sheet, ThermoFisher Scientific, 2019

[48] Safety Data Sheet, ThermoFisher Scientific, 2019

[49] Safety Data Sheet, ThermoFisher Scientific, 2019

Table 8: Exposure limits of the EU, UK and IRE for N-Methyl-2-pyrrolidone (99%) uptake through the skin.[50]

	European Union	**United Kingdom**	**Ireland**
STEL[51] [ppm]	20 ppm 15 min	20 ppm 15 min	20 ppm 15 min
STEL [mg·m^3]	80 mg·m^{-3} 15 min	80 mg·m^{-3} 15 min	80 mg·m^{-3} 15 min
TWA[52] [ppm]	10 ppm 8 hr	10 ppm 8 hr	10 ppm 8 hr
TWA [mg·m^3]	40 mg·m^{-3} 8 hr	40 mg·m^{-3} 8 hr	40 mg·m^{-3} 8 hr

Furthermore, NMP was included in 2018 in **REACh Annex XVII** and may only be marketed and used from May 2020 if compliance with certain exposure limits can be ensured.

Although NMP is classified as hazardous in the above regulations, we support the approval of the use of NMP in the small emission values and under the described safety measures in the process equipment.[53]

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[50] Safety Data Sheet, ThermoFisher Scientific, 2019

[51] Short-Term Exposure Limit

[52] Time Weighted Averages

[53] 1-Methyl-2-pyrrolidone, Registration Dossier – European Chemicals Agency, 2020.

5 Summary and Outlook

In this report, based on the current industrial production process and state of research, the elimination or substitution of NMP within the manufacturing process of lithium-ion batteries is considered to be not feasible in the near future. .

In Summary, it can be stated that an elimination through new technologies is currently not possible due to the reasons elaborated in this report. A substitution of NMP by a more environmentally friendly solvent can only be implemented if LFP is used as cathode material. However, LFP has a lower specific capacity and average voltage compared to NMC, making it unsuitable for use in the future electric vehicle market. It should also be noted that the TRL level for NMP is the highest possible at TRL9. The TRL levels for processes with other solvents in the cathode production, however, are all below TRL5, which indicates that the process is not yet fully developed and may involve unknown risks. One reason for this is that the processes have currently only been evaluated on a laboratory scale.
Since the cathode production with NMP as a solvent is an established process, the environmental risk can be management by certain precautions named in this report.

The intent of the UK Battery Industrialisation Centre is to develop and establish manufacturing technologies of lithium ion batteries associated with the automotive or other industries. It is well understood and similar to that experienced within the Pharmaceutical and Aerospace industries where confidence in any change to a known industrial process is inherently time consuming due to the certification and approval principles. This applies directly to the present research into the elimination or substitution of NMP within the Lithium Ion battery industry.

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