WORLD CLASS HEALTH & SAFETY EVENT

Michigan Safety Conference

Using Direct Reading Instruments to Measure Airborne Concentrations of Chemicals during Battery Manufacturing

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FIND YOUR SAFETY

MINDSET / MOTIVATION / INNOVATION

BEV Safety

94 Years - Find Your Safety __________!

INTRODUCTION

- Case study to share what we’ve learned about measuring airborne concentrations chemicals used in battery manufacturing

- Today’s presentation is based on our experience with lithium-ion battery research and manufacturing

    - Battery manufacturing processes
    - Battery chemicals
    - Measuring battery chemicals in real-time

HISTORICAL PERSPECTIVE

Electric Model T 1914 prototype

- Lead acid batteries

Ford Ranger 1998-2002

- NiMH batteries

Ford C-Max hybrid 2003 -2019

Ford Focus Electric 2011-2018

- Lithium-Ion batteries

LITHIUM-ION BATTERY RESEARCH & MANUFACTURING

CURRENT STATE

- Ongoing battery research at Dearborn R&E Center
- Ford Ion Park pilot plant in Romulus, MI opened in 2024
- Currently purchase batteries from suppliers such as LG and SK

NEAR FUTURE

New battery plants:

- **Blue Oval – SK (BOSK)**
- Joint venture with SK-On
- Glendale, KY and Stanton, TN
- Lithium Nickel Manganese Cobalt (NMC) batteries

- **Blue Oval Battery Park (BOBPM)**
- Marshall, Michigan
- Wholly-owned subsidiary
- Technology licensed from CATL
- Lithium Iron Phosphate ($LiFePO_4$) batteries

COMPARISON OF LITHIUM-ION BATTERY CHEMISTRY

Five Common Types of Lithium-Ion Batteries

Key Active Material	Lithium-Iron Phosphate	Lithium Nickel Manganese Cobalt Oxide	Lithium Manganese Oxide	Lithium Nickel Cobalt Aluminum	Lithium Titanate
Technology Short Name	LFP	NMC	LMO	NCA	LTO
Cathode	$LiFePO_4$	$LiNi_xMn_yCo_{1-x-y}O_2$	$LiMn_2O_4$ (spinel)	$LiNiCoAlO_2$	variable
Anode	C (graphite)	C (graphite)	C (graphite)	C (graphite)	$Li_4Ti_5O_{12}$
Safety					
Power Density					
Energy Density					
Cell Costs Advantage					
Lifetime					
BESS Performance					

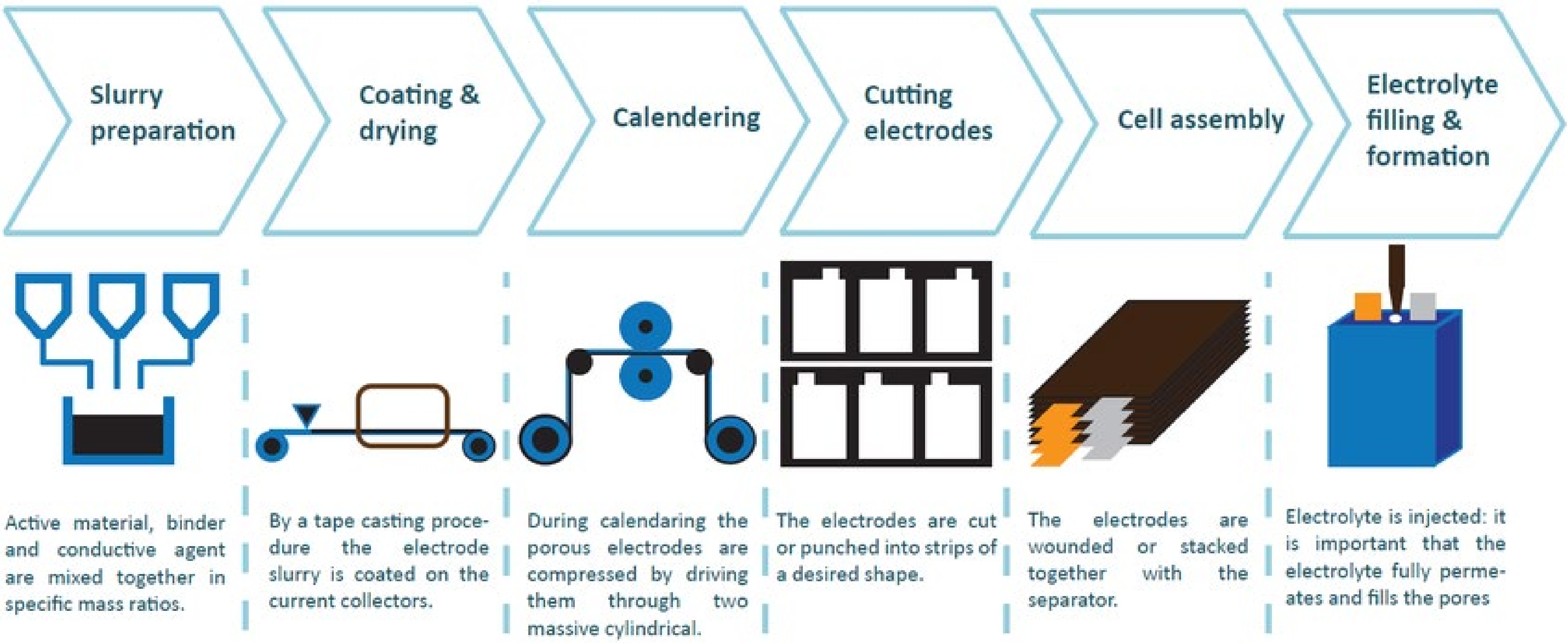
Source: International Renewable Energy Agency (IRENA), 2017

COMPARISON OF LITHIUM-ION BATTERY FORMATS

Cylindrical cell	Prismatic cell	Pouch cell
		
• Small size (e.g. 18650 type (ø 18 mm, height 650 mm)) • Hard casing • Low individual cell capacity • Build in safety features • Comparably cheap	• Hard casing • Large size • High individual cell capacity	• Soft casing • Large size • High individual cell capacity • Geometrical deformation during (dis-)charging

https://www.grepow.com/blog/prismatic-vs-pouch-vs-cylindrical-lithium-ion-battery-cell.html

BATTERY MANUFACTURING OVERVIEW



Slurry Preparation

Electrode manufacturing

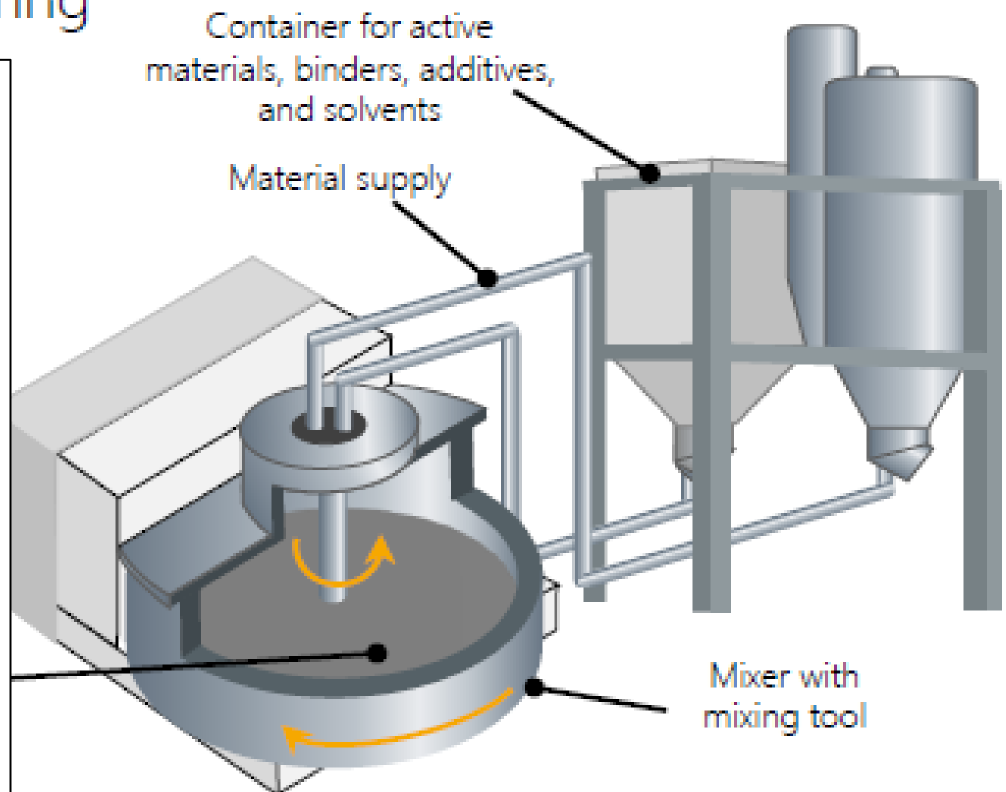
Separate processes for anode and cathode

<u>Step 1:</u>

Dry component mixing

<u>Step 2:</u>

Adding solvent to create slurry



Cell assembly | Cell finishing

https://vdma-industryguide.com/batteryproduction/downloads

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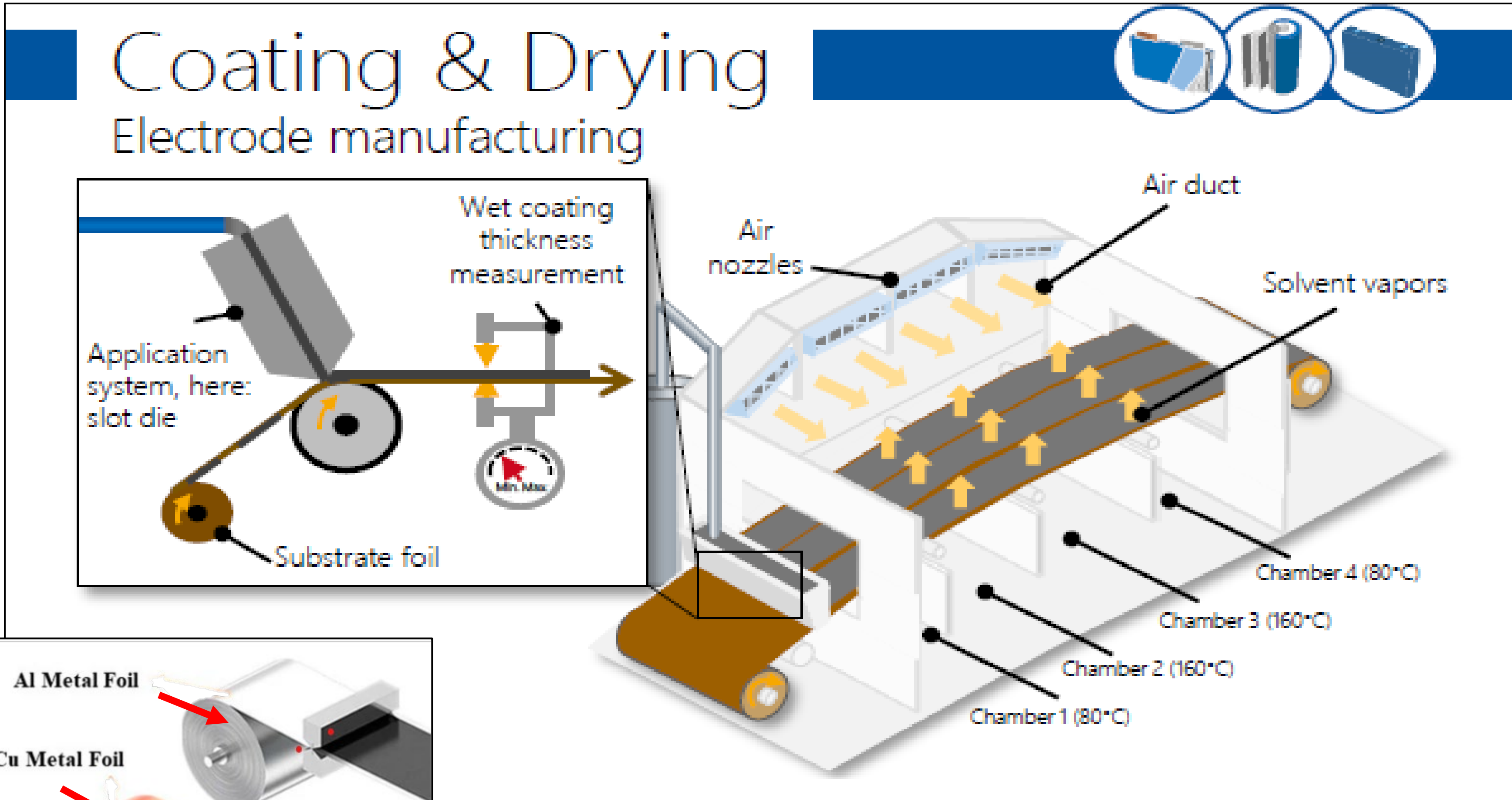

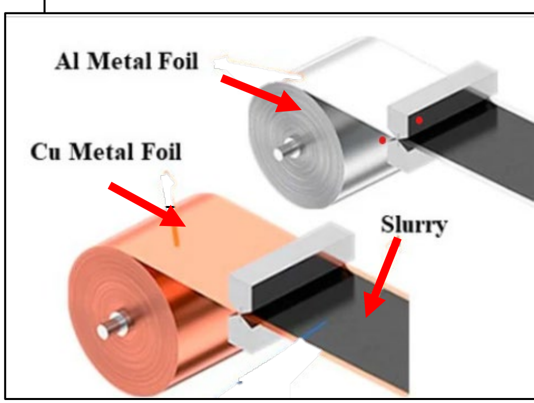

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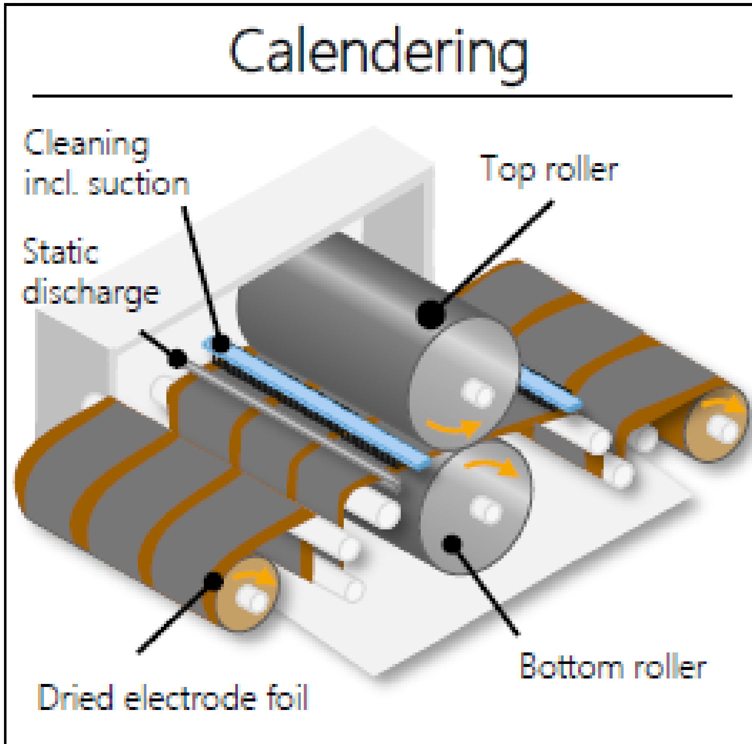
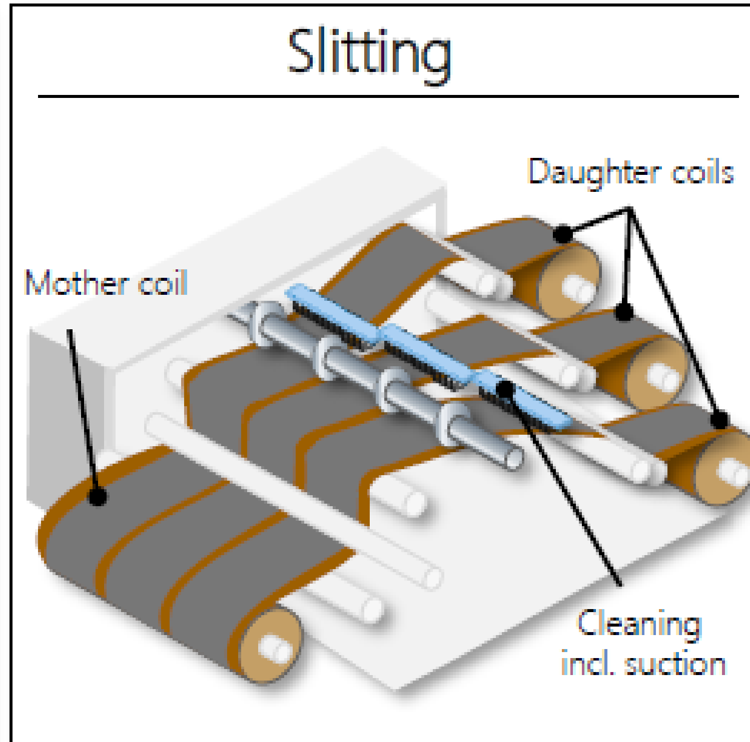
Calendering & Slitting

Electrode production





Cell assembly

Cell finishing

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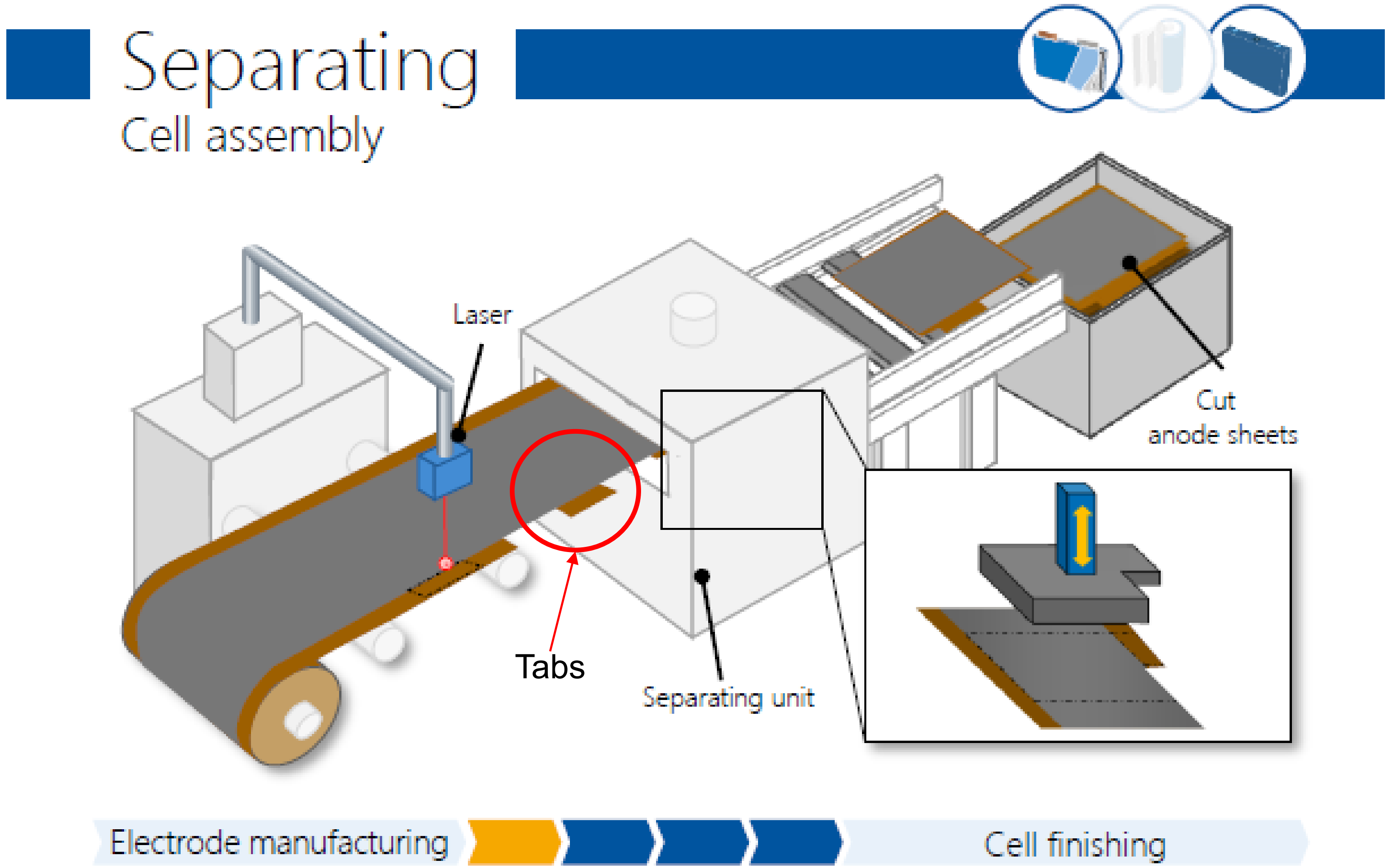

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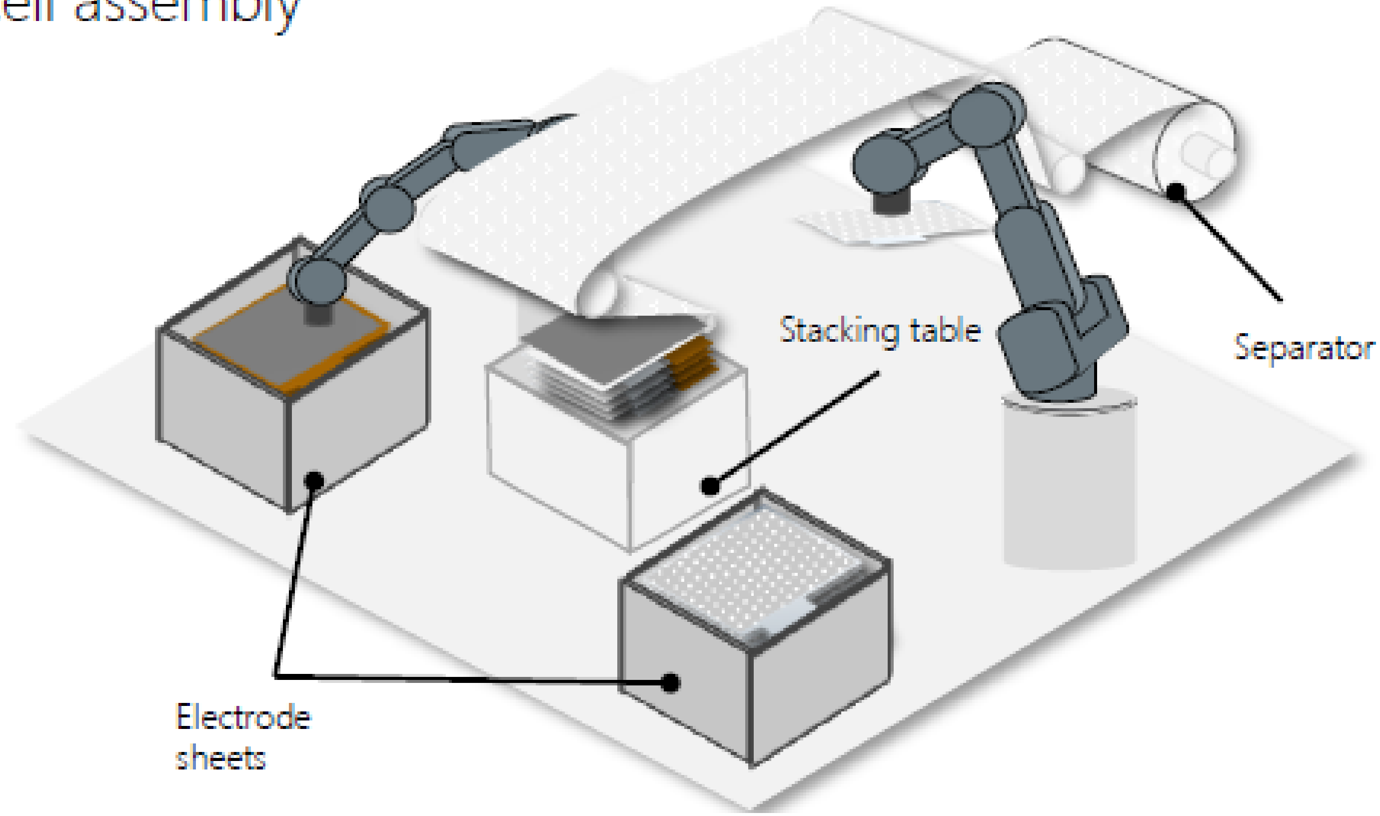
Stacking

Cell assembly



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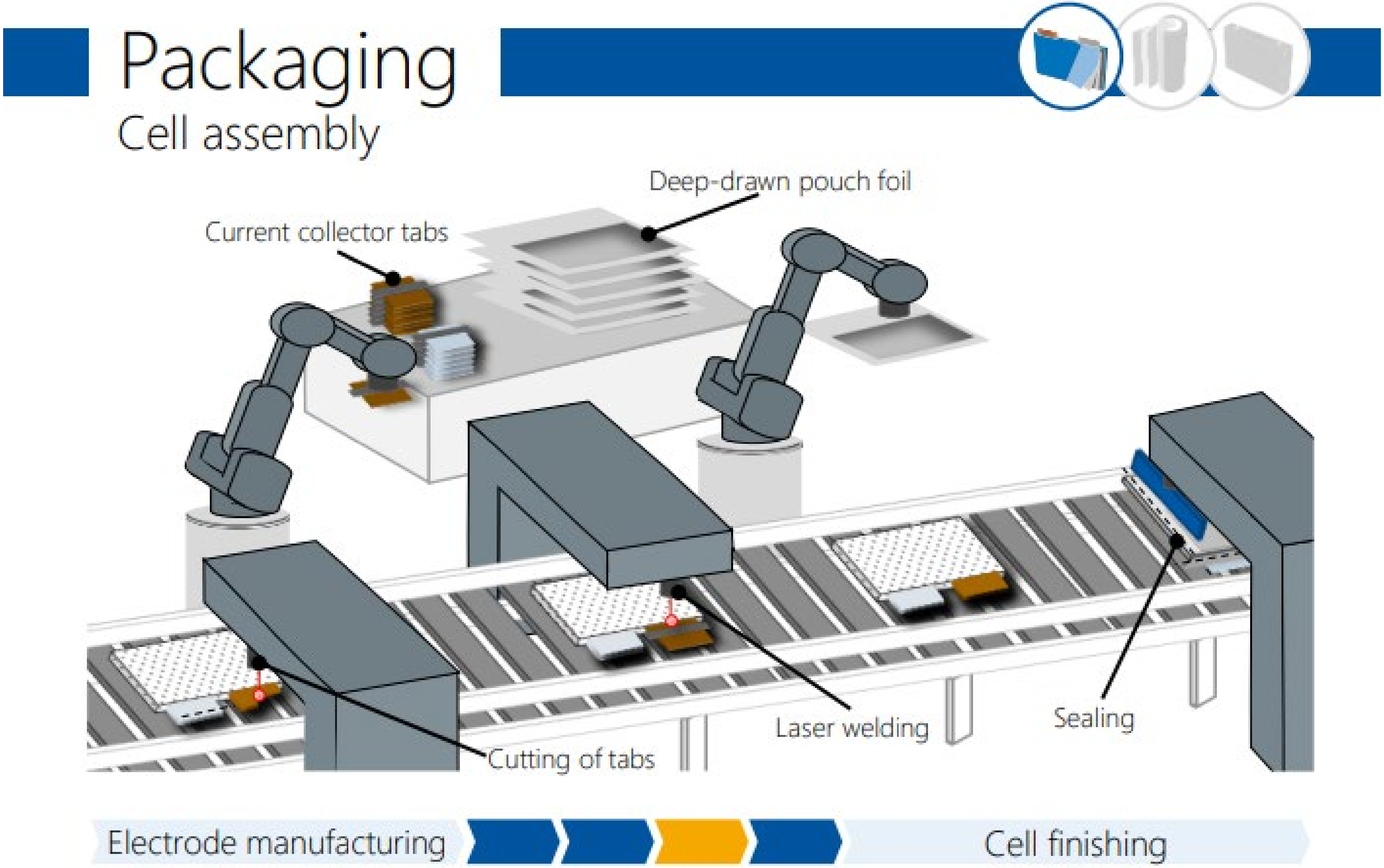

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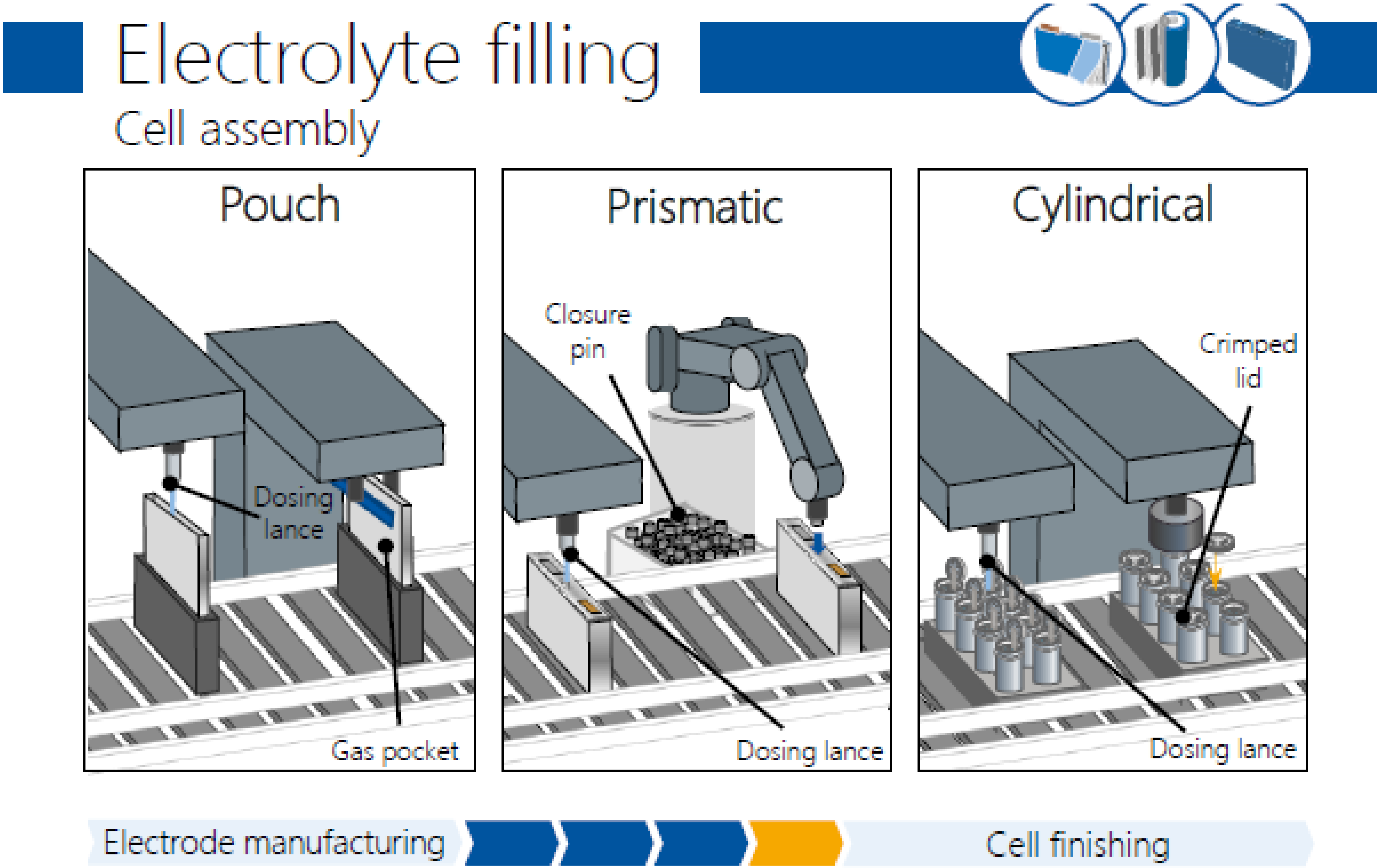

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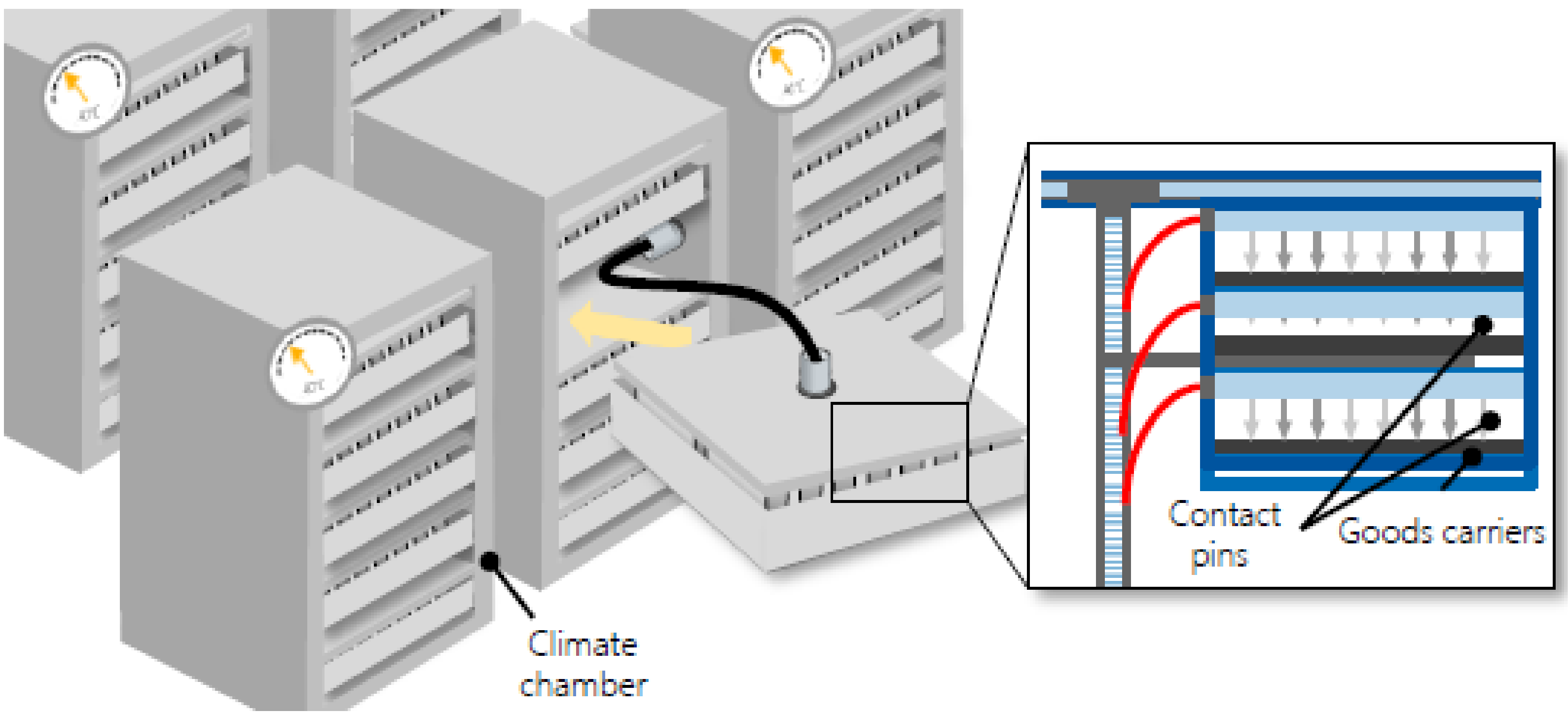
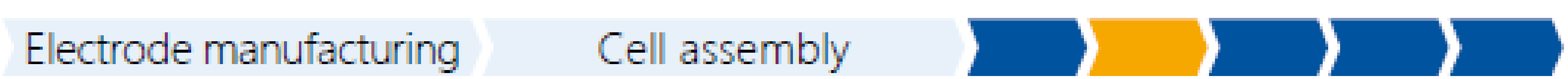
Formation

Cell finishing





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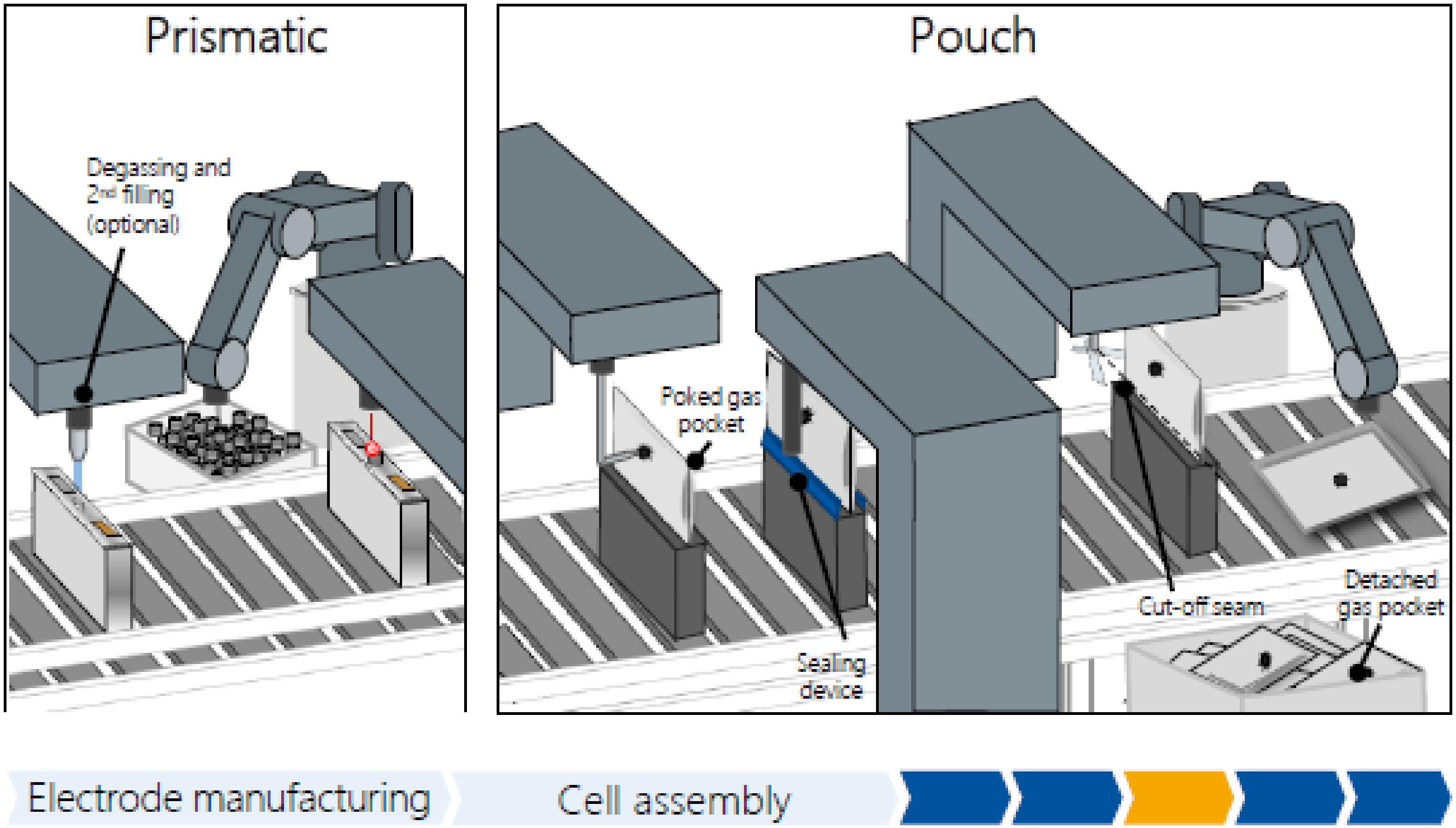
BATTERY MANUFACTURING OVERVIEW

Degassing

Cell finishing



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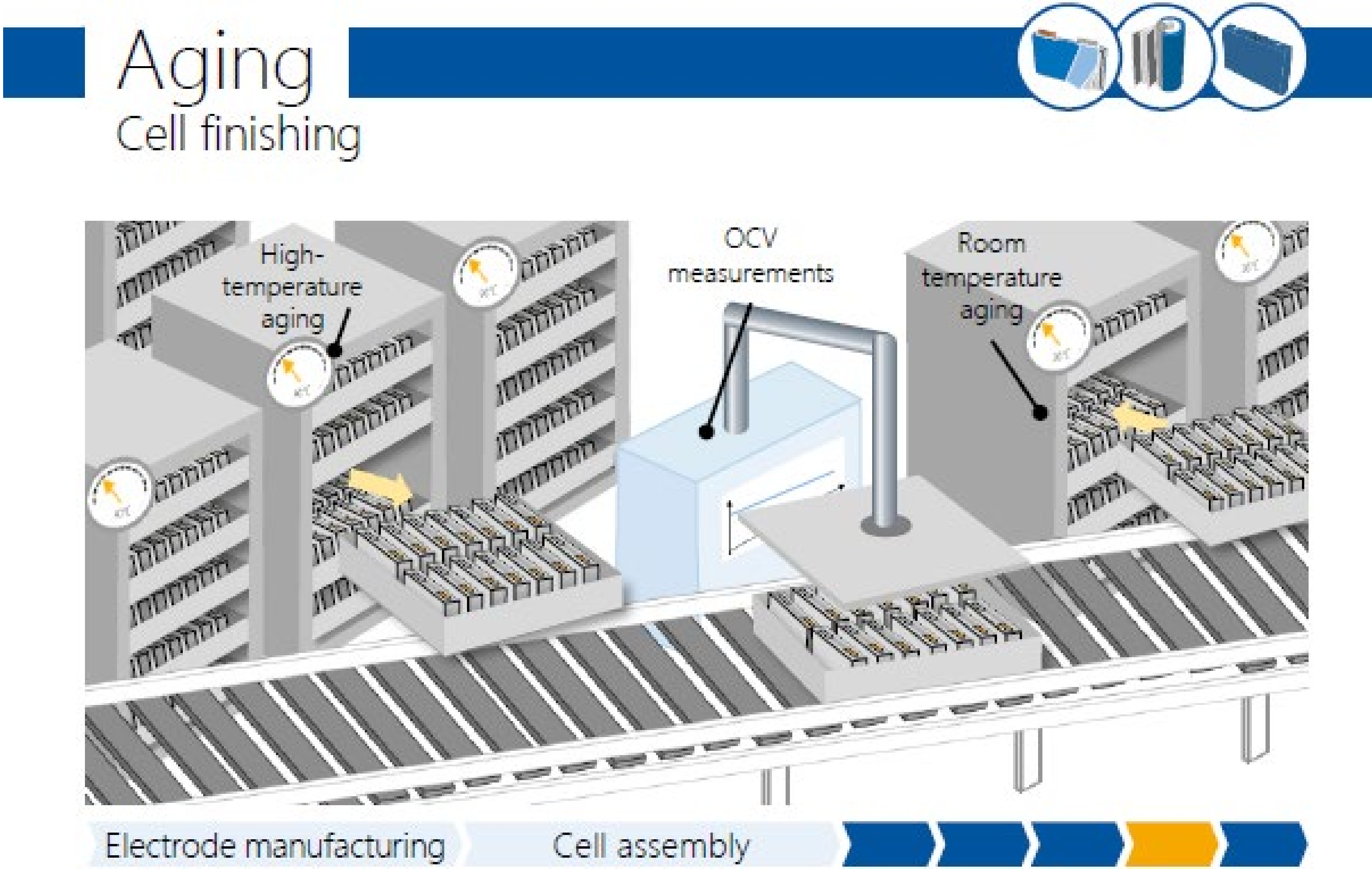

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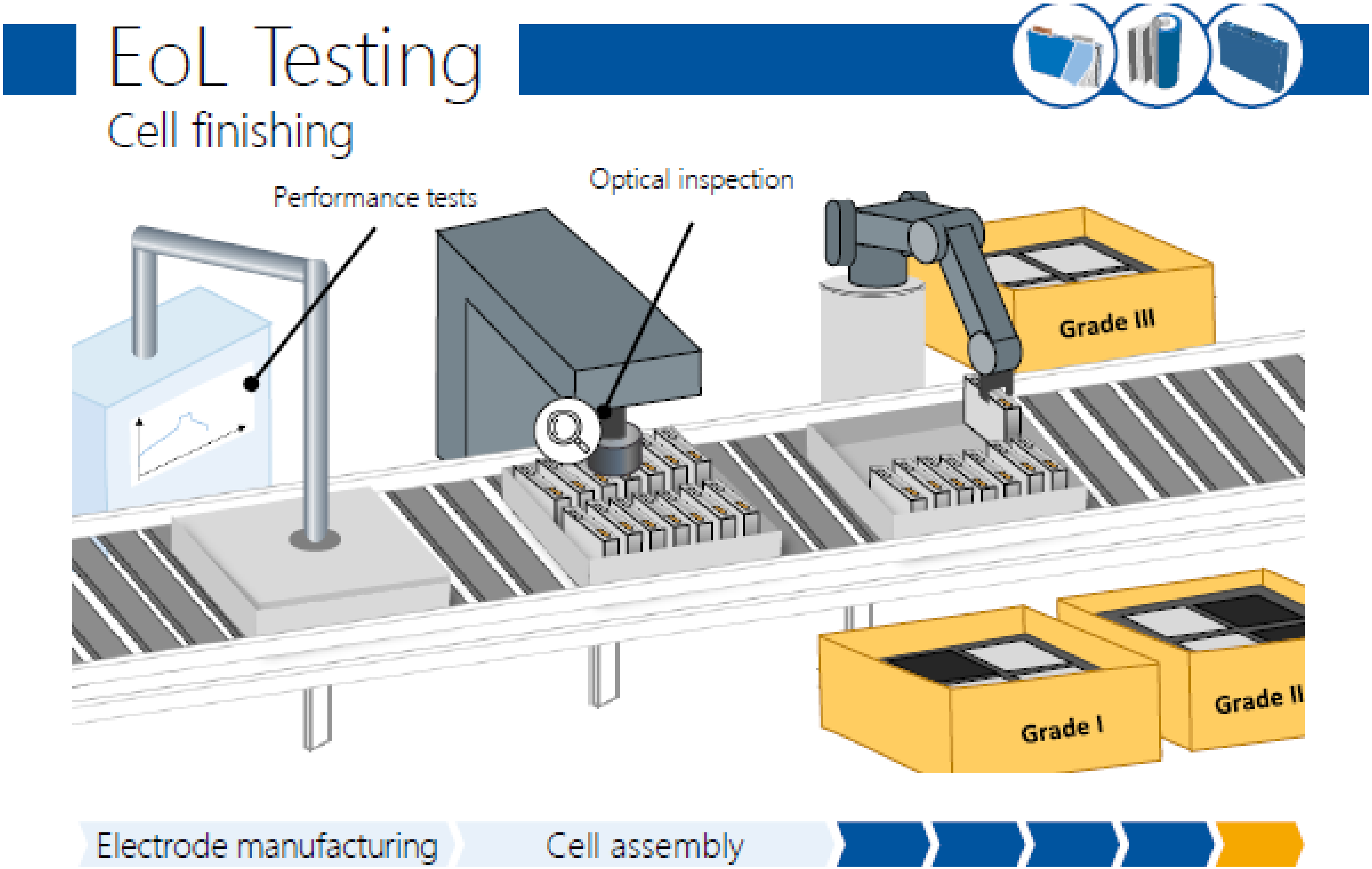

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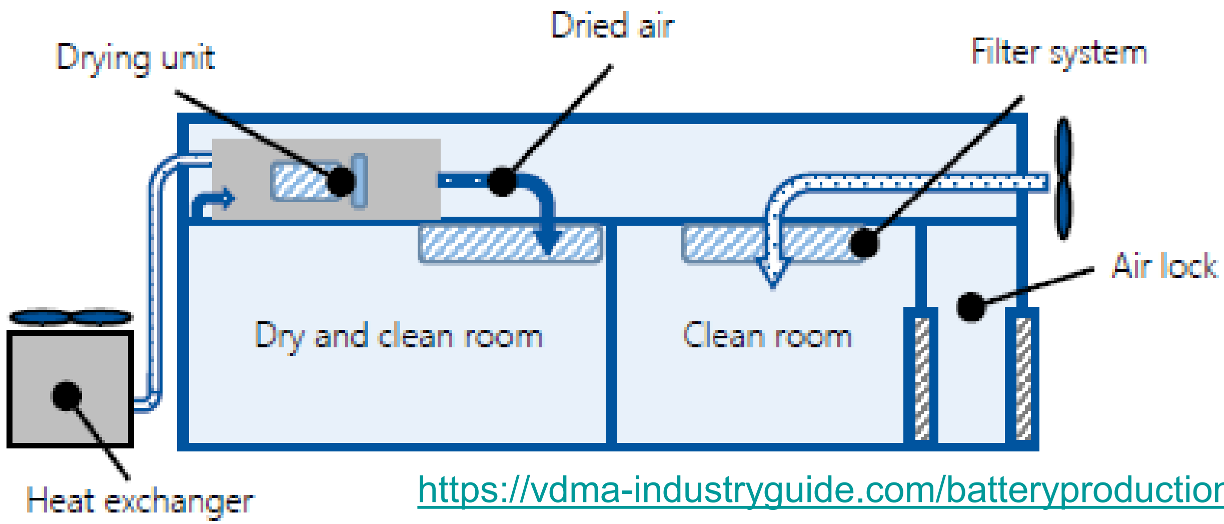
Process Environment



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Clean room: PPE for the protection of process integrity

Dry room: may be <0.05% RH

TYPICAL BATTERY MANUFACTURING CHEMICALS – ANODE

Photo: Graphite Central

Powdered Components*
- Graphite

Solvent*
- De-ionized water

Metal Foil*
- Copper

*Typical anode components; specific materials may vary by manufacturer.

https://vdma-industryguide.com/batteryproduction/downloads

TYPICAL BATTERY MANUFACTURING CHEMICALS – ANODE

- Anode materials are relatively low toxicity
- Worker exposures can be determined using standard IH sampling methods

Substance	CAS #	Form	Exposure Limit*	Notes	IH Sampling Method
Graphite	7782-42-5	Particulate	2 mg/m^3	Respirable Particulate	NIOSH 0600 Gravimetric
Copper foil	7440-50-8	Particulate	0.2 mg/m^3 1 mg/m^3	Fume Dust	NIOSH 7303 ICP
De-ionized Water	7732-18-5	Liquid	NA	Non-toxic	NA

*Threshold Limit Values (TLVs) published by the American Conference of Governmental Industrial Hygienists (ACGIH)

TYPICAL BATTERY MANUFACTURING CHEMICALS – CATHODE

<u>Powdered Components*</u>

- Lithium Nickel Manganese Cobalt Oxide

OR

- Lithium Iron Phosphate (LiFePO4)

<u>Solvent*</u>

- N-Methyl Pyrrolidone (NMP)

<u>Metal Foil*</u>

- Aluminum

*Typical cathode components; specific materials may vary by manufacturer.

$$LiNi_xMn_yCo_yO_2$$

$$LiFePO_4$$

Photo: https://www.chinafuran.com/uploads/201714518/n-methyl-pyrrolidone-nmp45140380463.jpg

https://vdma-industryguide.com/batteryproduction/downloads

TYPICAL BATTERY MANUFACTURING CHEMICALS – CATHODE

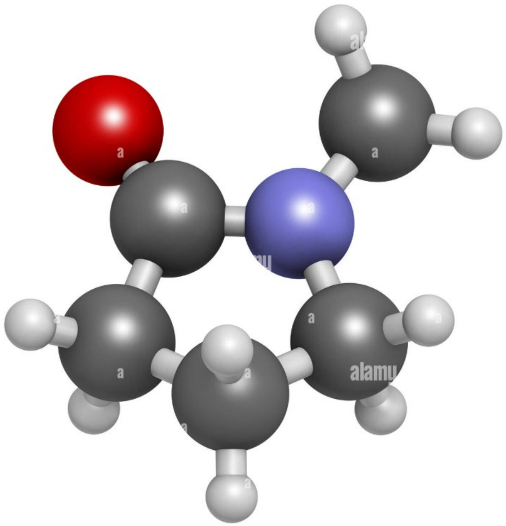
Substance	CAS #	Form	Exposure Limit*	Notes	IH Sampling Method
NMC ($LiNiMnCoO_2$)	346417-97-8 182442-95-1	Particulate	0.1 mg/m^3	EPA NCEL**	NIOSH 0500 Gravimetric NIOSH 7303 ICP
Lithium	7439-93-2	Particulate	NA		
Nickel, (Insoluble inorganic cpds)	7440-02-0	Particulate	0. 2 mg/m^3	Inhalable fraction	NIOSH 0500 NIOSH 7303 ICP
Manganese, as Mn (Insoluble inorganic cpds)	7439-96-5	Particulate	0.02 mg/m^3 0.1 mg/m^3	Respireable fraction Inhalable fraction	NIOSH 0500/0600 NIOSH 7303 ICP
Cobalt, as Co (Inorganic cpds)	7440-48-4	Particulate	0.02 mg/m	Inhalable fraction	NIOSH 0500 NIOSH 7303 ICP
Lthium Iron Phosphate	15365-14-7	Particulate	2.4 mg/m^3 1 mg/m^3	EPA NCEL** Iron Salts, as Fe***	NIOSH 0500 Gravimetric NIOSH 7303 ICP
Aluminum foil (metal and insoluble cpds)	7429-90-5	Particulate	1 mg/m^3	Respirable fracton	NIOSH 0600 NIOSH 7303 ICP
N-Methyl Pyrrolidone	872-50-4	Liquid	Further Discussion on Next Slide		

*Threshold Limit Values (TLVs) published by American Conference of Industrial Hygienists

** [Non-confidential List of TSCA New Chemical Exposure Limits, (updated March 2018) | US EPA]

Comparison of NMP exposure limits:

Occupational Exposure Limit - NMP	ppm	mg/m^3
American Conference of Governmental Industrial Hygienists Threshold Limit Values (TLVs)	Not established	Not established
US Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL)	Not established	Not established
Michigan OSHA PEL	Not established	Not established
Kentucky and Tennessee OSHA State Plans	Not established	Not established
California OSHA PEL	**1 ppm**	**4 mg/m^3**
Occupational Alliance for Risk Science (formerly AIHA) Workplace Environmental Exposure Limit (WEEL)	15 ppm 8-hour 30 ppm 15-minute	60 mg/m^3 8-hour 120 mg/m^3 15-minute
Ontario Occupational exposure limits	97 pppm	400 mg/m3
European REACH Legislation Derived No Affect Level (DNEL)	3.4 ppm	14 mg/m^3
European Union, European Chemicals Agency Occupational Exposure Limits	10 ppm 8-hour 20 ppm 15-minute	40 mg/m^3 8-hour 80 mg/m^3 15-minute
German MAK	20 ppm 8-hour 40 ppm 15-minute	82 mg/m^3 8-hour 164 mg/m3 8-hour



Standard IH Exposure Assessment Methods:

- Charcoal sorbent tube or passive dosimeter badge with analysis by gas chromatography (NIOSH Method 1302)

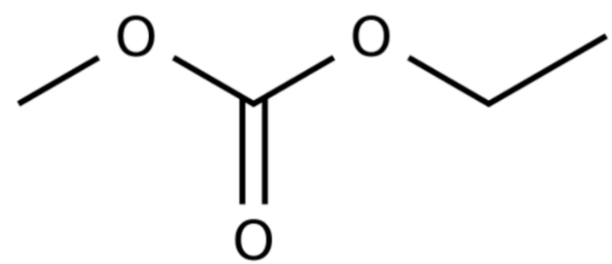
BATTERY MANUFACTURING – TYPICAL ELECTROLYTE FILL

After the battery cell has been assembled, liquid electrolyte is added to the cell.

Each manufacturer has a proprietary recipe, but all lithium-ion batteries* contain:

- A mixture of alkyl carbonates
- Lithium fluoride salts, such as lithium hexafluorophosphate

<u>Common Carbonates</u>
- Ethylene Carbonate
- Ethyl Methyl Carbonate
- Diethyl Carbonate
- Dimethyl Carbonate
- Propylene Carbonate



Li^{+} PF_6^{-}

Lithium Hexafluorophosphate

*Solid state batteries have a different chemistry.

BATTERY MANUFACTURING – TYPICAL ELECTROLYTE FILL

Substance	CAS #	Form	Exposure Limit	Notes	IH Sampling Method
Ethylene Carbonate	96-49-1	Dissolved solid	No Published Exposure Limits		Bureau Veritas (next slide)
Ethyl Methyl Carbonate	623-53-0	Liquid			
Diethyl Carbonate	105-58-8	Liquid			
Dimethyl Carbonate	616-38-6	Liquid			
Propylene Carbonate	108-32-7	Liquid	2 ppm	German MAK*	
Lithium Hexafluorphosphate	21324-40-3	Dissolved solid	2.5 mg/m^3	As fluoride	NIOSH 7906 Ion Chromatography

* German MAK Commission IFA - Databases: GESTIS Limit Values - Germany - MAK

For more information about the toxicology of alkyl carbonates, refer to a reliable source, such as the National Institute for Occupational Safety & Health (NIOSH) or the European Chemicals Agency (ECHA)

BATTERY MANUFACTURING – ELECTROLYTE FILL

IH Sampling & Analytical Method – Bureau Veritas, Novi Lab

	Reporting Limit
Dimethyl carbonate (DMC)	4 mg/sample
Diethyl carbonate (DEC)	4 mg/sample
Ethylmethyl carbonate (EMC)	4 mg/sample
Ethylene carbonate (EC)	20 mg/sample
Methyl propyl carbonate (MPC)	4 mg/sample
Propylene carbonate (PC)	4 mg/sample
Anasorb 747, 210 mg, SKC 226-81A	
50 mL/min	
Up to 8 hours	
Up to 24 L	
Ship cold, particularly for DMC to prevent storage migration	
28 days under ambient and refrigerated temperatures. DMC samples must be stored refrigerated to prevent storage migration. Best to recommend refrigerated storage for all analytes.	

DIRECT READING INSTRUMENTS FOR BATTERY CHEMICALS

- There are traditional IH sampling methods available for most of the chemicals used in battery manufacturing.
- However, samples must be submitted to a laboratory for analysis. Lab results typically take 2-14 days.
- In the event of an unplanned event, such as a leak or spill, that is a long time to wait for results
- A direct-reading instrument that can measure airborne concentrations in real time would be a valuable resource

“Is it safe to go back to work?”

Make that decision based on data.

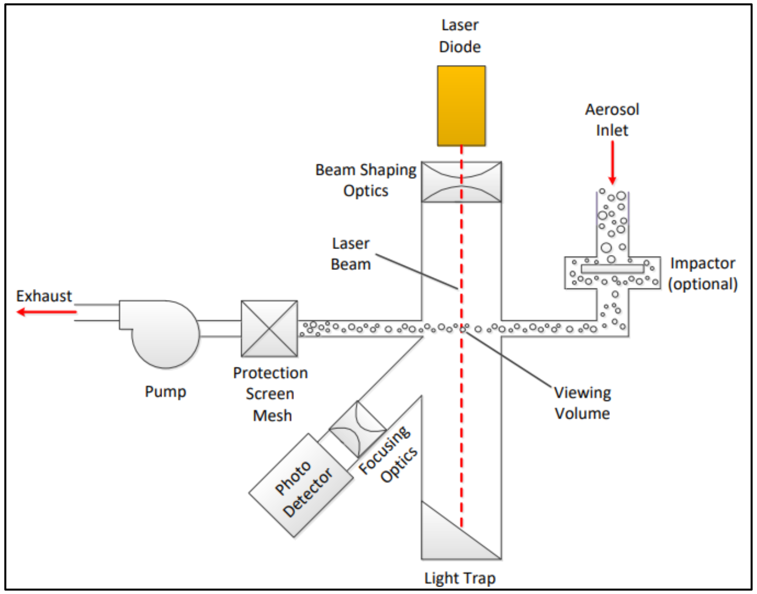
Objectives of Direct-Reading Instruments:

- Assess hazards following a spill and determine when it is safe to return to work
- Evaluate engineering controls and detect leaks
- Measure employee exposures during non-standard tasks to support selection of appropriate PPE

In most situations, a standard “four gas” meter will not provide any of these capabilities

PHOTOMETER FOR PARTICULATES

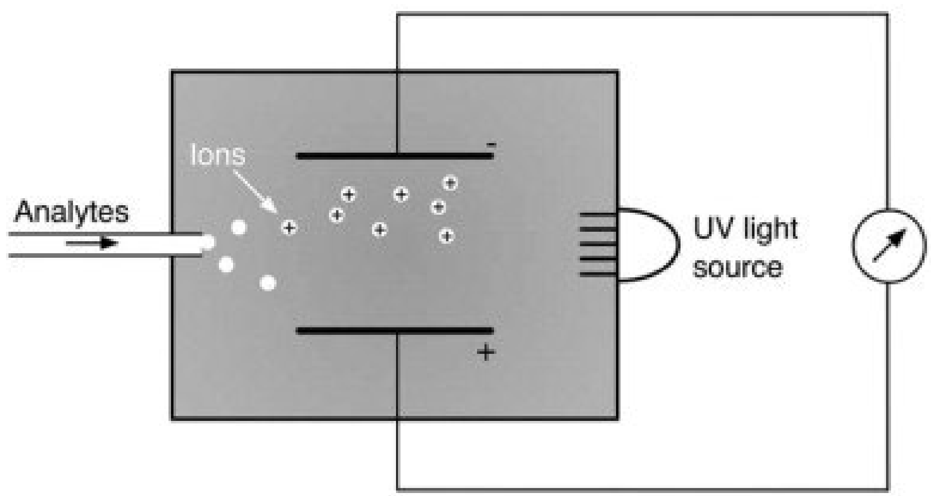
- Measures particles in the air as a function of light scattering
- Distinguish particle size, such as PM10, PM2.5, & PM1 using pre-screening device
- Detect particles > 1 um diameter
- Results affected by particle size and material properties
- Cannot identify specific substances
- Baseline ≠ zero



https://tsi.com/products/aerosol-and-dust-monitors/aerosol-and-dust-monitors

PHOTO IONIZATION DETECTOR (PID) FOR VOCs

- High-energy ultraviolet (UV) light ionizes molecules in a sample
- 9.8 eV, **10.6 eV**, 11.7 eV lamps
- Charged particles generate a measurable electric current which is proportional to the concentration of the detected compounds
- More sensitive than an LEL sensor



Photoionization Detector - an overview | ScienceDirect Topics

https://www.rae-gasmonitors.com/xxyy-minirae-3000-plus.html

PHOTO IONIZATION DETECTOR (PID) FOR VOCs

- Calibrated with isobutylene
- Non-specific: responds to all gases that are present in the air and can be ionized.
- Can be programmed to read in terms of a specific substance such as N-Methyl Pyrrolidone
- Conversion factors published by manufacturer, based on how the instruments responds to specific chemicals relative to isobutylene

Substance	Conversion Factor 10.6 eV
Isobutylene (calibration)	1
Ethylene Carbonate	NR
Ethyl Methyl Carbonate	18
Diethyl Carbonate	7
Dimethyl Carbonate	70
Propylene Carbonate	62
NMP	0.8 - 0.9
Ethanol	10 - 11
Xylene	0.39 - 0.54

Higher value = lower sensitivity relative to isobutylene

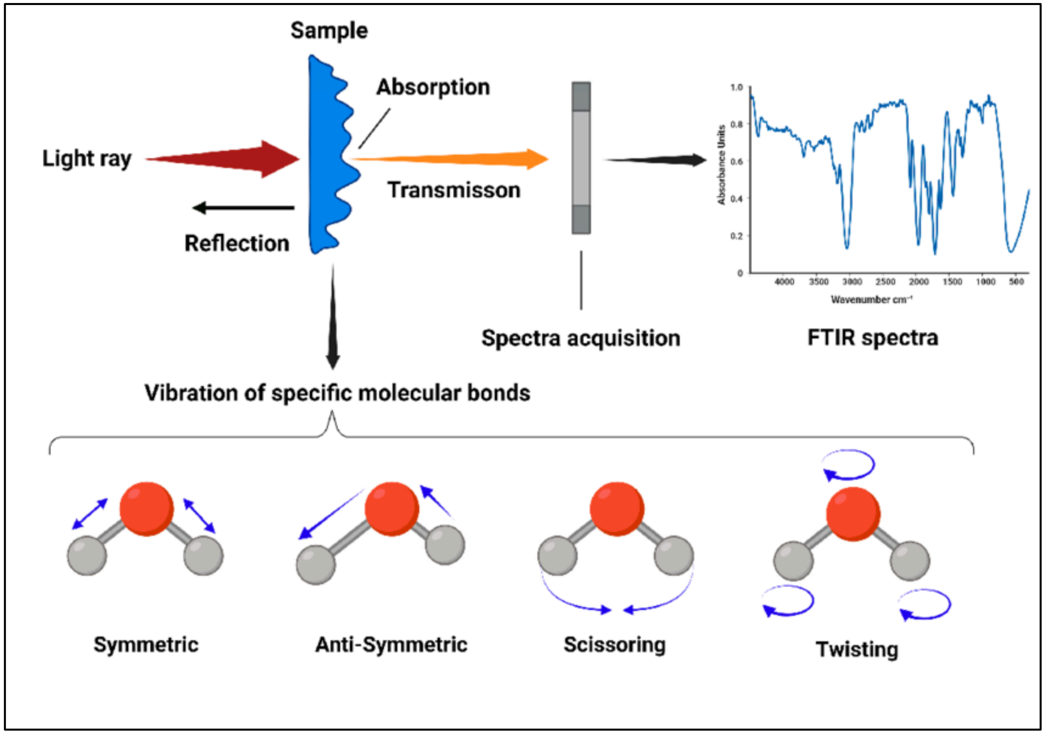
PID Lessons Learned

- Substances with large correction factors will be hard to measure because of interference from other substances
- Don’t assume that other chemicals aren’t present

CASE STUDY #1 – PID LESSONS LEARNED

- An air leak in an exhaust duct resulted in an odor during cathode coating using NMP
- As a precaution, production was suspended, and personnel were evacuated from the area
- Personnel wearing PAPRs used the PID to take measurements for NMP
- The results of these measurements were up to 10 ppm, above the 1 ppm Ford OEL for NMP.
- Area samples were also collected using passive dosimeters and sent to the laboratory for NMP.
- Laboratory results subsequently showed concentrations of NMP ranged from 0.51 – 0.79 ppm, much lower than the PID measurements

FOURIER TRANSFORM INFRA-RED SPECTROMETER



https://www.researchgate.net/figure/nfrared-spectroscopy-measures-the-interaction-of-infrared-radiation-with-matter-Upon_fig1_381354000

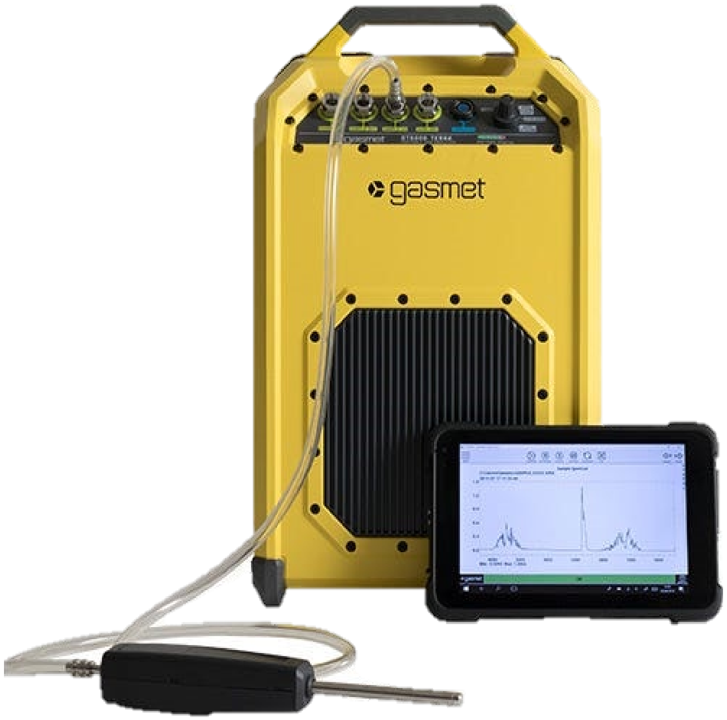
When **Infra-red (IR)** radiation is passed through an air sample, some radiation is absorbed

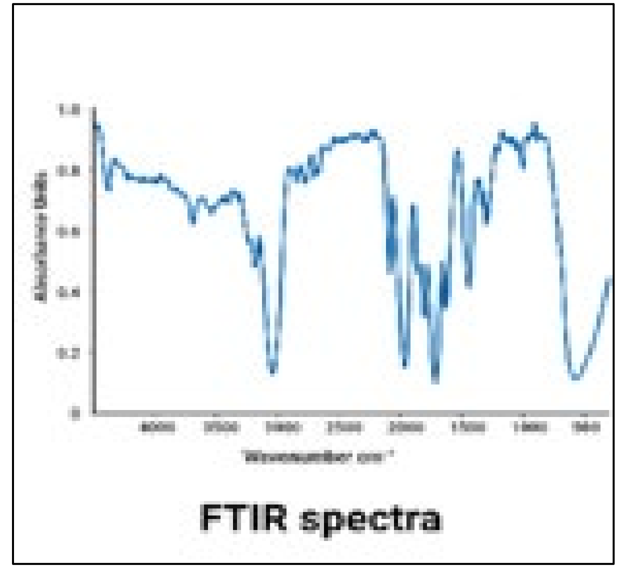
The wavelengths that are absorbed depend on the bond energies of the chemical molecules in the air sample

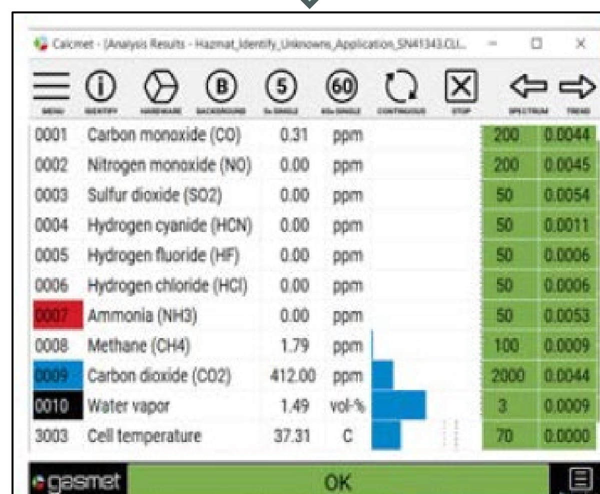
The signal received at the detector is converted to a spectrum representing a molecular ‘fingerprint’ of the sample by a mathematical function called a Fourier Transform.

The resulting spectrum can be used to identify and quantify specific chemical substances very accurately, without interference from other substances

INTRODUCING THE GASMET GT5000 PORTABLE FTIR







Software interprets the spectrum and displays the concentration of chemicals in parts per million

Typical range = 0.01 – 100 ppm

Gasmet.com

GASMET GT5000 PORTABLE FTIR

“Take sample and tells us what’s in it.”

GASMET GT5000 PORTABLE FTIR PROS & CONS

- **Future proof - additional gases can be added to the database**
- **No calibration required**
- **Simple operation**
- **FTIR spectrometry is proven technology**
- **Low detection limit: 0.01 ppm**
- **“Almost” real time – 5, 20, or 60 seconds per sample**

- **High initial investment ($60-75K)**
- **Ultra-pure nitrogen required to purge instrument**
- **Too large to be used for personal samples**

?

Portability – backpack, not hand-held

CASE STUDY #2: COMPARISON OF NMP MEASUREMENTS:

Location	Number of Measurements	FTIR[1]		PID[2]		Lab Samples[3]	
		Range (ppm)	Mean (ppm)	Range [4] (ppm)	Mean [4] (ppm)	Duration (Minutes)	Results (ppm)
Area Location #1	9	0.49 - 0.80	0.64	7.1 - 7.6	7.4	448	0.57
Area Location #2	20	0.54 - 0.85	0.72	6.2 - 10.6	8.9	448	0.50
Area Location #3	27	0.51 - 0.88	0.70	4.0 - 9.8	7.7	452	0.43
Area Location #4	16	0.44 - 0.82	0.68	6.0 - 9.8	7.8	NA	

Notes:
(1) GASMET GT5000 FTIR
(2) RKI GX6000
(3) Samples collected using Assay Technology 546AT Organic Vapor Passive Dosimeter; analyzed by Bureau Veritas, Novi, MI
(4) PID results corrected for NMP using 0.9 CF provided by the manufacturer .

- **Ford OEL for NMP = 1 ppm**
- **FTIR data < 1 ppm (safe to work)**
- **PID Data >> 1 ppm (evacuate area)**
- **Lab data was consistent with FTIR results***

*Laboratory data provides a time-weighted average concentration during the entire sampling period, while each measurement made with direct-reading instruments was a point-in-time measurement taken in one-minute intervals.

WHY DO WE GET HIGH READINGS FOR NMP WITH THE PID?

1. Are other chemicals present?

Ethanol
- Used in laboratories
- One source identifies ethanol as reaction product of NMP with water/humidity
- But CF=11: 11 ppm ethanol would increase the PID reading by only 1 ppm

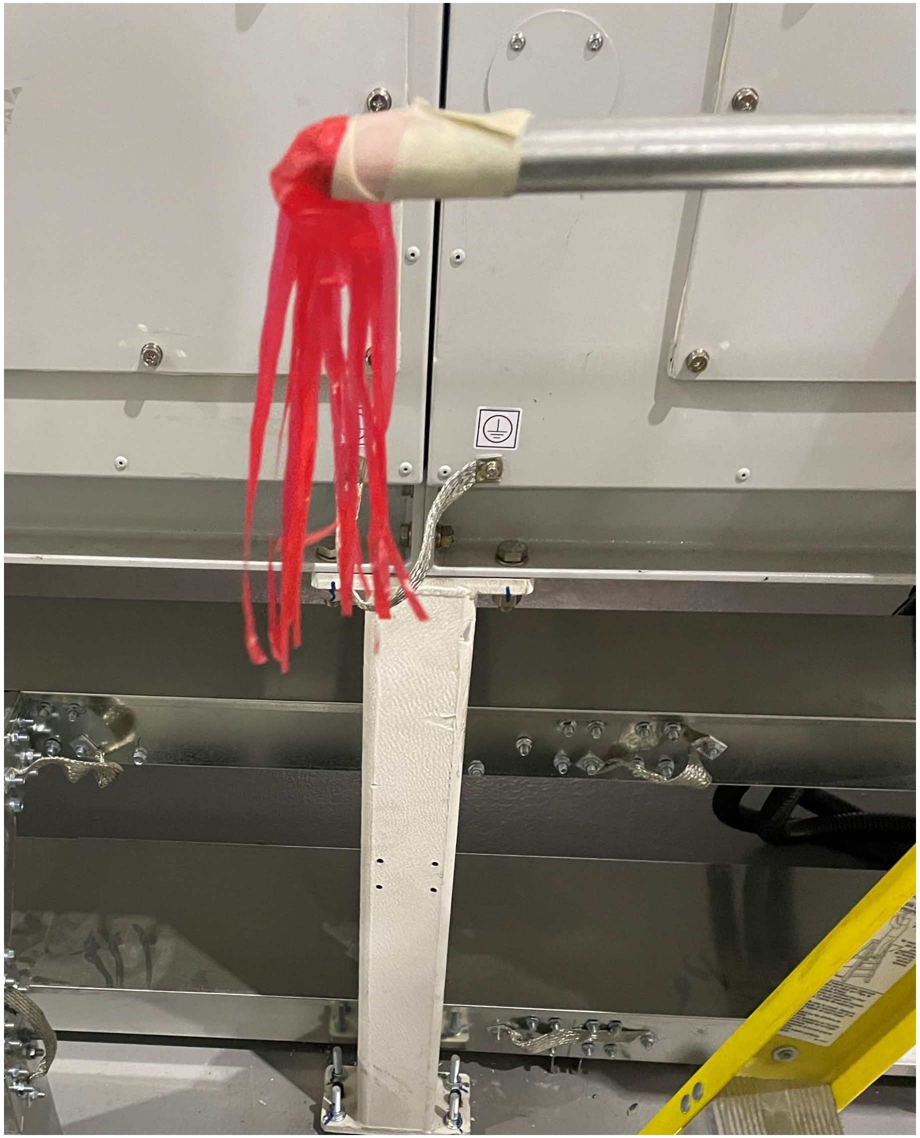
NMP Decomposition Products
- Further research required

2. Is there something else causing high measurements?

PID literature identifies sources of LOW measurements, but not high:
- Oxygen
- High humidity
- Methane

A FINAL THOUGHT – DON'T OVERLOOK LOW TECH SOLUTIONS

"Directional Air Flow Leak Tester"
(DAFLT)



Questions?

Thank You for your attendance.