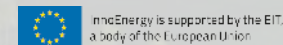




October 2021
VSAMS PROJECT

SUPPORTED BY



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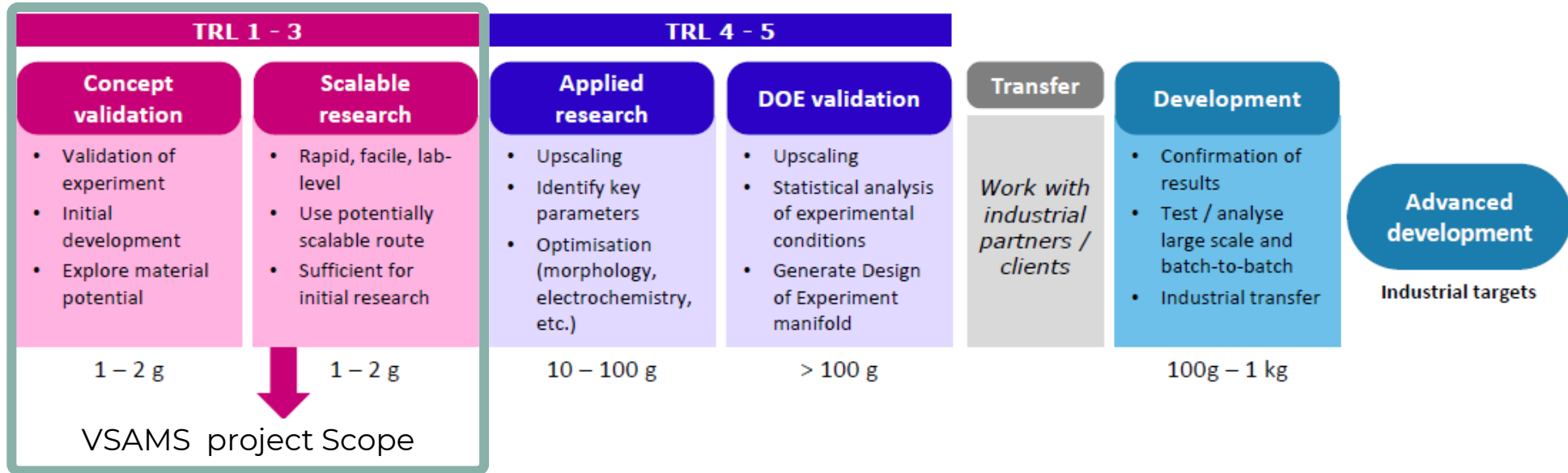
SUMMARY OF THE VSAMS PROJECT

1

CONTEXT

VSAMS Project Scope:

Overall material development:



To accomplish this TRL 1 to 3 evaluation, the following tasks were carried out:

- Characterization and comparison of **Verkor** and reference MnSO₄ precursors (**V-MnSO₄** and **REF-MnSO₄**)
- Synthesis and characterization of NMC622 using **reference** salt (**REF-NMC**)
- Synthesis and characterization of NMC622 using **Verkor** salt (**V-NMC**)
- Formulation and coin cell tests of the 2 different NMC622 (**REF-NMC** and **V-NMC**)



VSAMS PROJECT ORGANIZATION

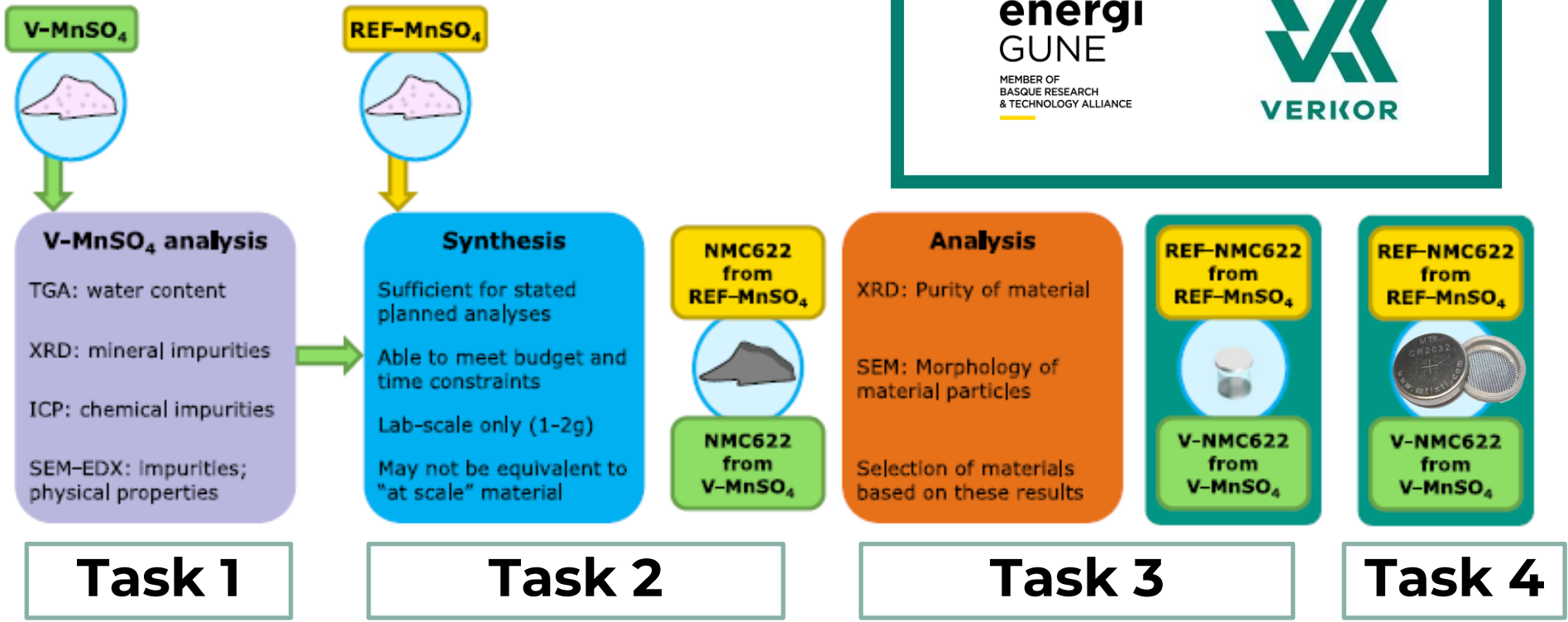
1

Overall Project organization

Cooperation between:

**CIC
energi
GUNE**

MEMBER OF
BASQUE RESEARCH
& TECHNOLOGY ALLIANCE



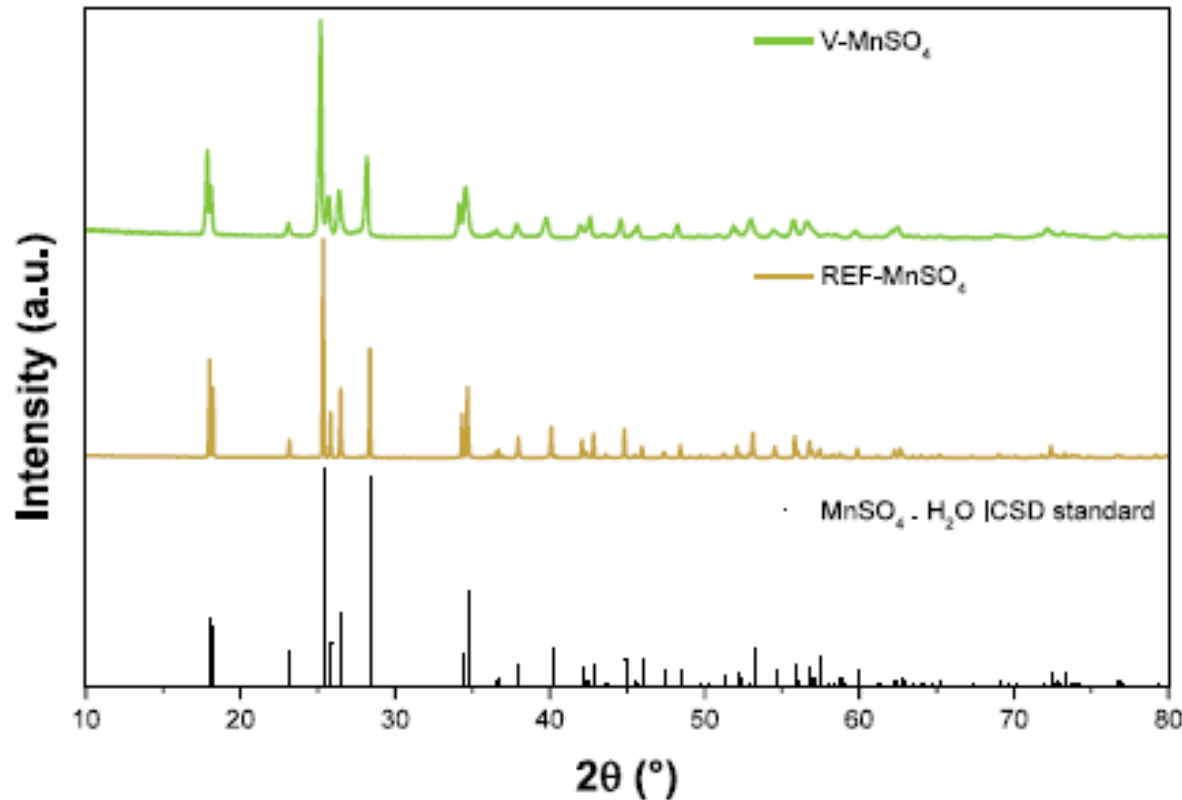


SUMMARY OF THE TASK 1

2

Task 1 : 1.1 XRD

XRD analysis (crystalline structure)

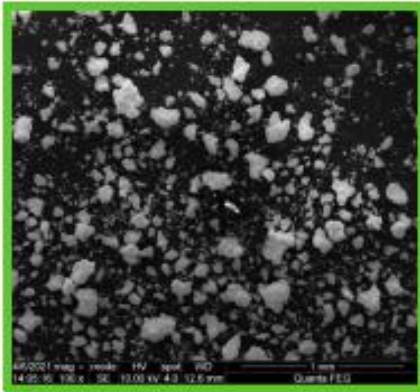


- No crystalline impurities detected in samples
- Pattern in keeping with that reported for MnSO₄ · H₂O
- Validates purity of salt ✓

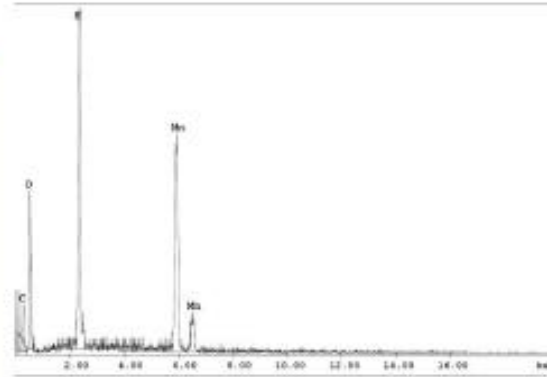
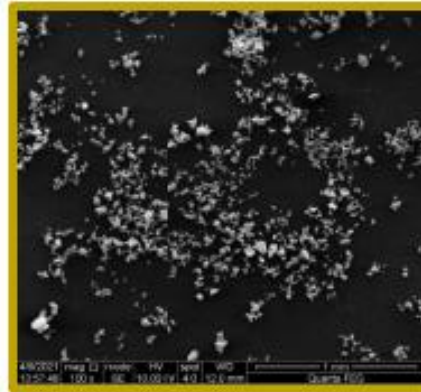
Task 1 : 1.2 SEM & EDX

SEM and EDX (physical and elemental characteristics)

V-MnSO₄



REF-MnSO₄



- SEM: V-MnSO₄ exhibits slightly "agglomerated" nature
- EDX: no other elements detected
- Validates salt composition and purity ✓

Task 1 : 1.3 ICP

ICP (elemental analysis characteristics)

- Based on concentration of elements:

	Mn (ppm)	S (ppm)
Theoretical (for $\text{MnSO}_4 \cdot \text{H}_2\text{O}$)	100	58.36
REF- MnSO_4	100	58.48 (± 1%)
V- MnSO_4	100	58.01 (± 1%)

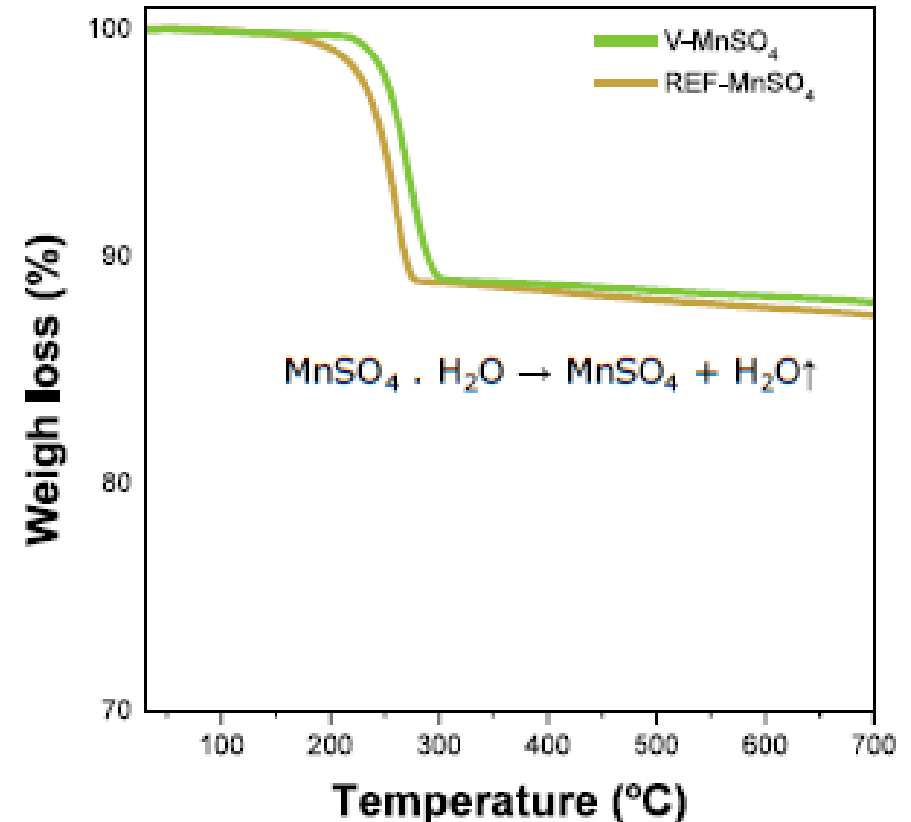
- Values in keeping with those expected for $\text{MnSO}_4 \cdot \text{H}_2\text{O}$
- No other elements detected
- Validates salt composition and purity ✓

Task 1 : 1.4 TGA

TGA (hydration characteristics)

- TGA analysis reveals mass loss with temperature
- Analysis of V-MnSO₄ is consistent with monohydrate [1].
- Implies V-MnSO₄ exists in monohydrate form – i.e. MnSO₄.H₂O

Validates salt hydration, and enables mass calculations for synthesis ✓



Task 1 : Conclusion remarks

Summary:

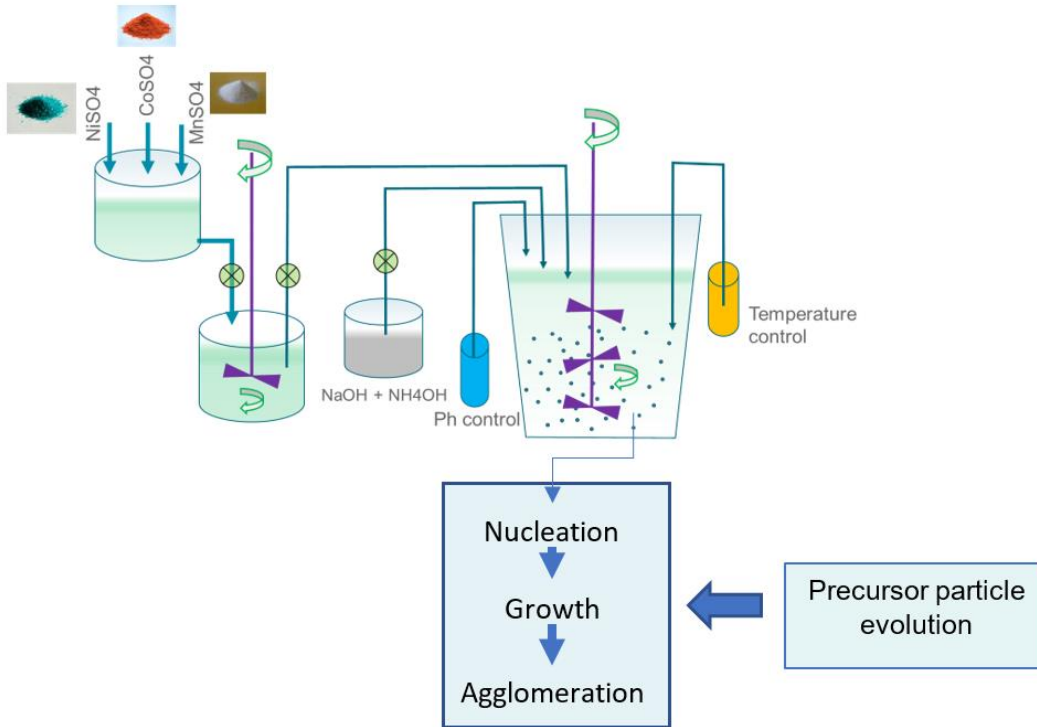
- Analysis of V-MnSO₄ indicates material is pure, and implies composition is manganese sulphate monohydrate
- Versus comparable material tests, those results are very positive
- Characteristics sufficiently identified to enable use in Task 3 (synthesis of NMC622)



VSAMS PROJECT TASK 2

3

Task 2 : Material synthesis



Material synthesis done using classic method

Overall process ok

Reference and V samples material done.

To be used in Task 3 : material analysis

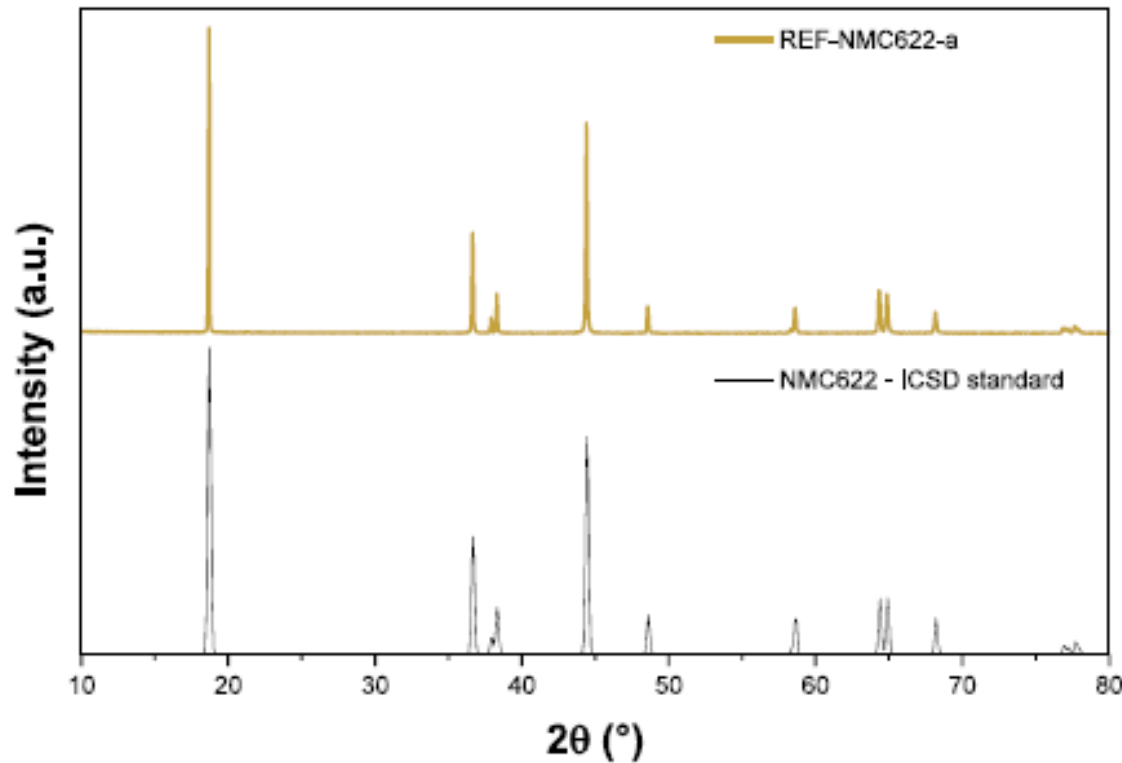


VSAMS PROJECT TASK 3

4

Task 3 : XRD - Ref

XRD analysis (crystalline structure)

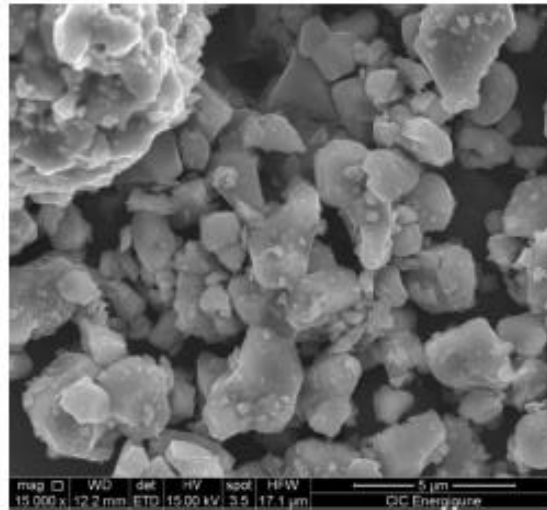
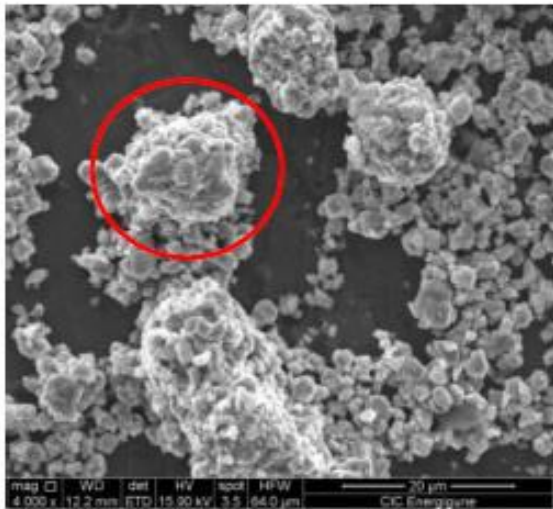


- No crystalline impurities detected in samples
- Pattern in good agreement with that reported for NMC622
- Scherrer equation (based on FWHM) suggests crystallite size ca. 84 nm

Task 3 : SEM and EDX - Ref

SEM and EDX (physical and elemental characteristics)

REF-NMC622-a



- SEM: powder consists of individual particles (<math>< 4 \mu\text{m}</math>). Appear to be areas where some particles may have aggregated.
- EDX: shows Ni:Mn:Co ratio of 6.2 : 1.7 : 2.1 – *i.e.* slight Mn deficiency

Task 3 : Summary on XRD, EDX and SEM for Ref

Summary and future activity planning:

- Analysis of REF-NMC622-a XRD indicates material is pure, and in good agreement with the literature.
- From EDX, it seems Mn deficient (*ca.* 1.7 instead of 2).

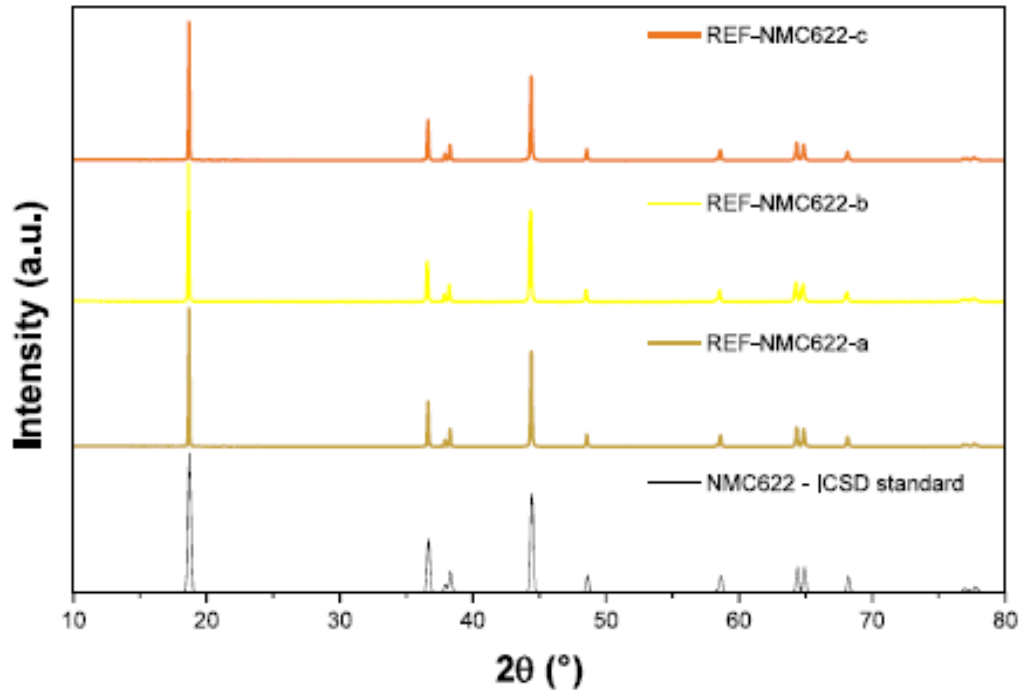
Does this require further action?

Possible actions:

- *Verify with ICP?*
 - *Optimise further?*
- From SEM, particles appear to be <4 μm , fairly angular with a moderate aspect ratio.

Task 3 : XRD Ref – reproducibility

XRD analysis (crystalline structure)

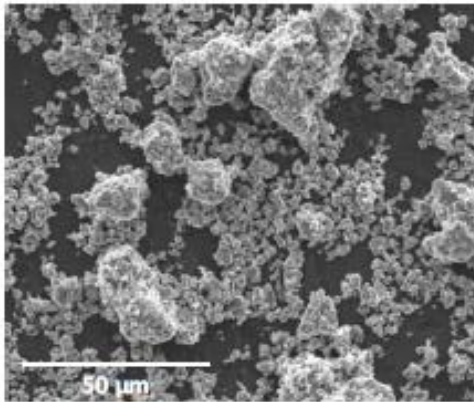


- No crystalline impurities detected in samples
- Patterns in good agreement with that reported for NMC622
- Patterns show good reproducibility between syntheses

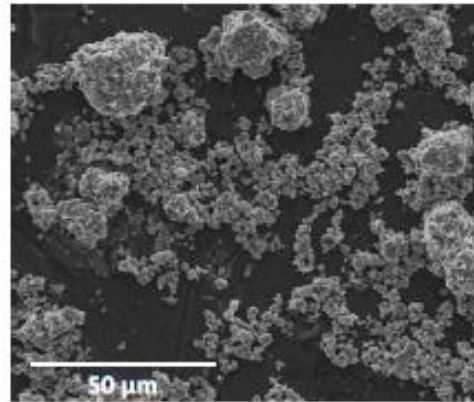
Task 3 : SEM and EDX Ref – reproducibility

SEM and EDX (physical and elemental characteristics)

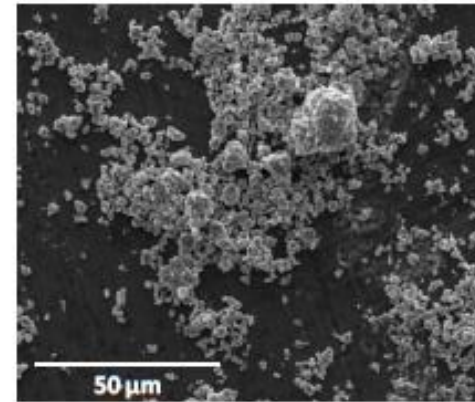
REF-NMC622-a



REF-NMC622-b



REF-NMC622-c



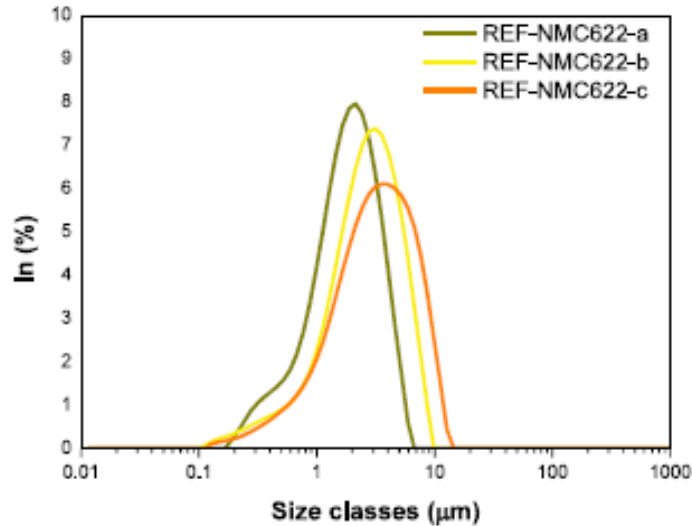
EDX	REF-NMC622-a	REF-NMC622-b	REF-NMC622-c
Ni	6.3	6.3	6.3
Mn	1.7	1.7	1.7
Co	2.0	2.0	2.0

Variations, but within instrumental error.

Planned ICP verification.

Task 3 : Mastersizer Ref (extra measure for powder size)

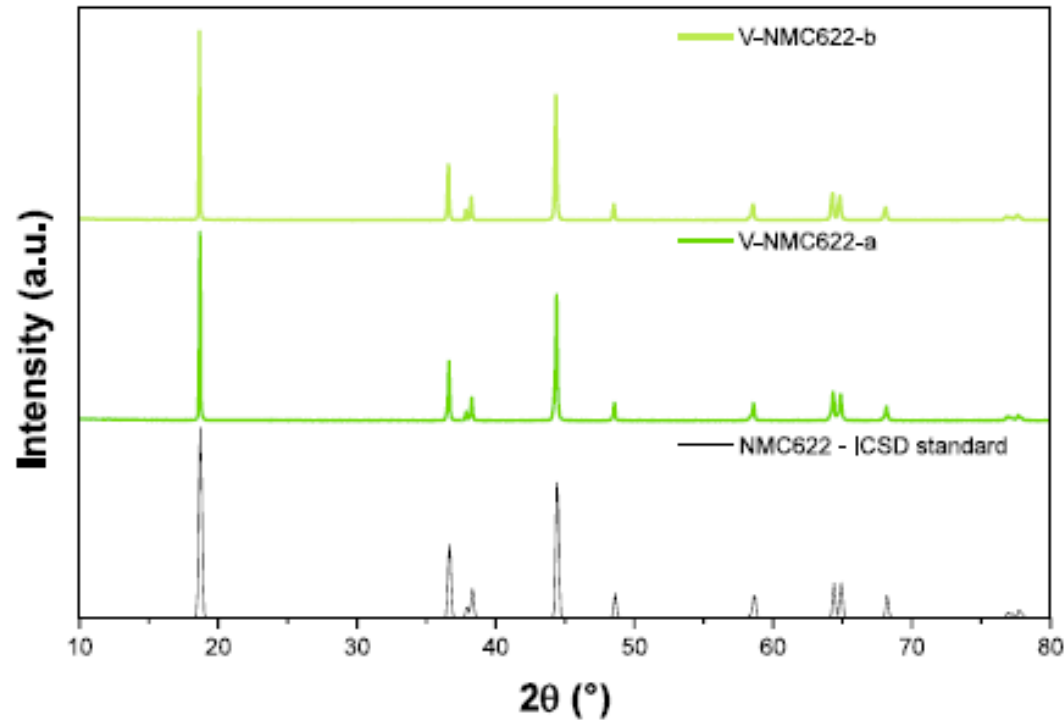
Mastersizer (physical size characteristics)



- Mastersizer: powder size analysis gives D_{50} of 2 - 4 µm (in keeping with SEM).
- While some differences, good reproducibility for lab-scale experiments (not in equilibrated tank reactor)

Task 3 : XRD for V sample

XRD analysis (crystalline structure)

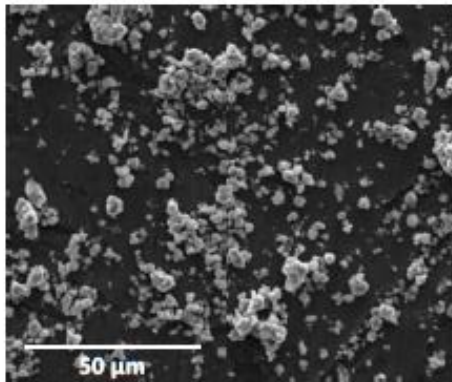


- No crystalline impurities detected in samples
- Patterns in good agreement with that reported for NMC622
- Patterns show good reproducibility between syntheses

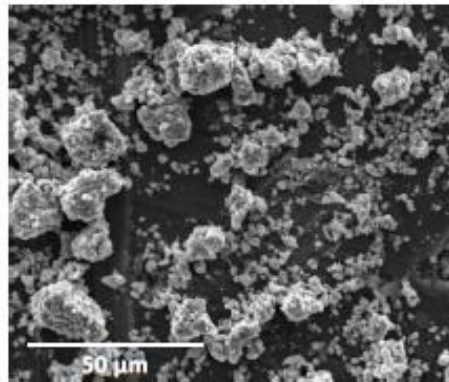
Task 3 : SEM and EDX for V Sample

SEM and EDX (physical and elemental characteristics)

V-NMC622-a



V-NMC622-b



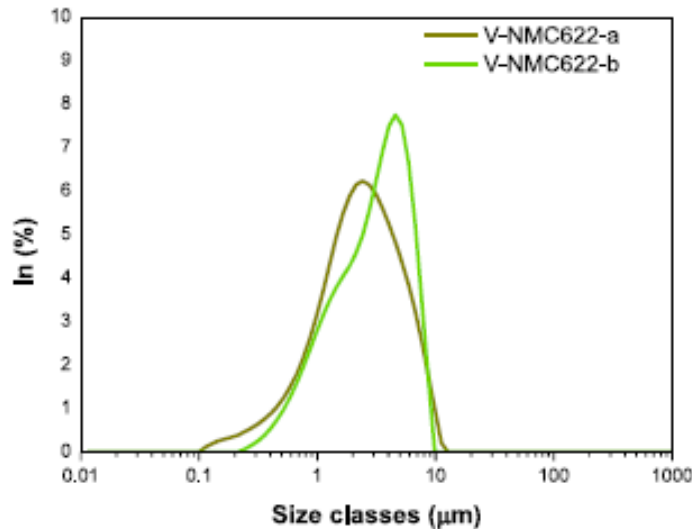
EDX	V-NMC622-a	V-NMC622-b
Ni	6.3	6.3
Mn	1.7	1.7
Co	2.0	2.0

Variations, but within instrumental error.

Planned ICP verification.

Task 3 : Mastersizer for V Sample

Mastersizer (physical size characteristics)



- Mastersizer: powder size analysis gives D_{50} of 2.5 - 3 μm (in keeping with SEM).
- While moderate reproducibility for lab-scale experiments, there are more noticeable differences between a and b. Work will continue with c (to be made), with a possibility to extend to d (time permitting) to determine if variations are common or anomalous.

Task 3 : ICP Ref and V Sample

ICP (elemental analysis characteristics)

- Based on concentration of elements:

REF-NMC622-b

Element	Cc ppm (theoretical)	Cc ppm (ICP)	%RSD	Stoichiometry
Ni	381.49	386.07	0.84	0.62
Mn	105.33	105.40	0.05	0.18
Co	124.01	124.70	0.39	0.20

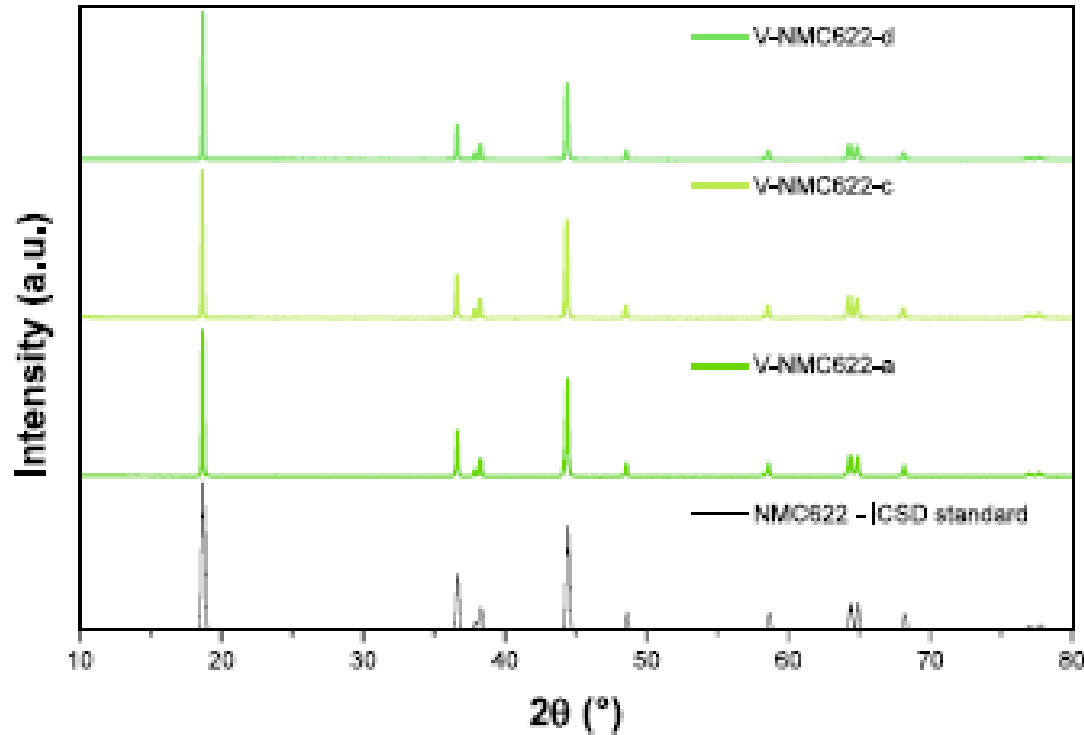
V-NMC622-a

Element	Cc ppm (theoretical)	Cc ppm (ICP)	%RSD	Stoichiometry
Ni	342.74	342.97	0.05	0.61
Mn	100.78	100.90	0.08	0.19
Co	113.57	113.50	0.04	0.20

- Values in keeping with those expected (based on target stoichiometry and EDX)
- No other elements detected
- Differences may be due to instrumental or weighing error, experimental conditions, etc. Further ICP to be carried out on remaining samples to identify if trend present.

Task 3 : XRD V Samples Reproducibility

XRD analysis (crystalline structure)

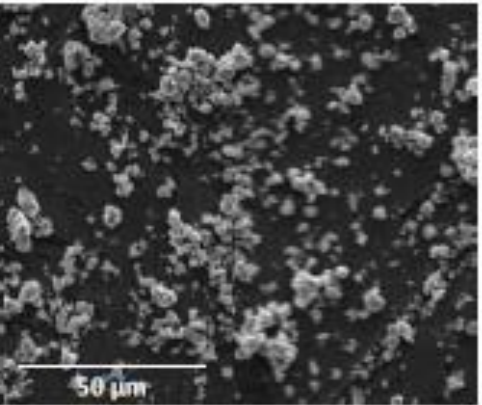


- No crystalline impurities detected in samples
- Patterns in good agreement with that reported for NMC622
- Patterns show good reproducibility between syntheses

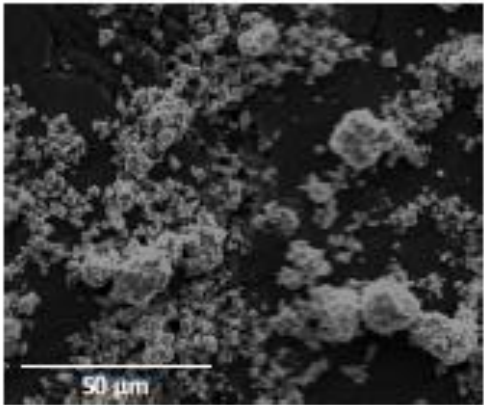
Task 3 : SEM and EDX V Sample - Reproducibility

SEM and EDX (physical and elemental characteristics)

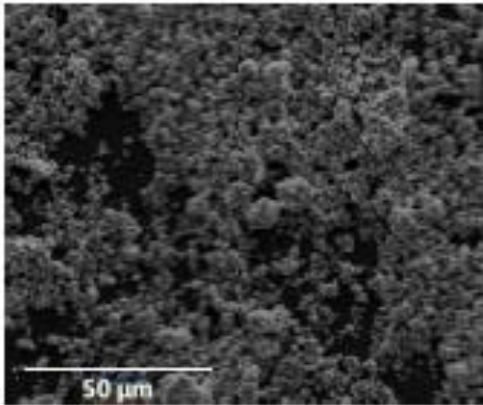
V-NMC622-a



V-NMC622-c



V-NMC622-d



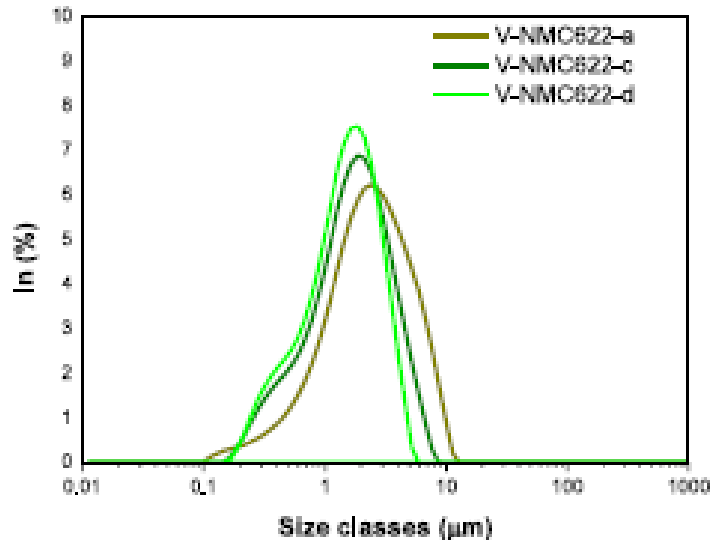
EDX	V-NMC622-a	V-NMC622-c	V-NMC622-d
Ni	6.3	6.3	6.3
Mn	1.7	1.7	1.7
Co	2.0	2.0	2.0

Variations, but within instrumental error.

Planned ICP verification.

Task 3 : Mastersizer for V Sample - reproducibility

Mastersizer (physical size characteristics)



- Mastersizer: powder size analysis gives D_{50} of 1.5 – 2.5 μm (in keeping with SEM).
- While some differences, good reproducibility for lab-scale experiments (not in equilibrated tank reactor). V-NMC622-b appears to have been an anomalous result, as discussed in previous report.

Task 3 : IPC

ICP (elemental analysis characteristics)

- Based on concentration of elements

	Li	Ni	Mn	Co
REF-NMC622-a	1.17	0.61	0.19	0.20
REF-NMC622-b	1.13	0.62	0.18	0.20
REF-NMC622-c	1.18	0.61	0.19	0.20
V-NMC622-a	1.14	0.61	0.19	0.20
V-NMC622-c	1.09	0.60	0.20	0.20
V-NMC622-d	1.09	0.61	0.19	0.20

- Li excess likely due to NMC content in pre-calcination intermediate being estimated from ideal composition. Future work could include more precise measurement (e.g. ICP) to enable accurate determination of lithiating agent requirements.

- Multielemental ICP revealed only contributions from these element.

Fe	Ca	Zn	Pb	Al	S
0.0000	0.0002	0.0008	0.0000	0.0050	0.0071
0.0000	0.0008	0.0007	0.0000	0.0077	0.0081
0.0000	0.0000	0.0009	0.0000	0.0033	0.0058
0.0000	0.0000	0.0001	0.0000	0.0039	0.0062
0.0001	0.0000	0.0007	0.0000	0.0071	0.0093
0.0000	0.0000	0.0008	0.0000	0.0053	0.0066

- Fe, Ca, Zn, Pb negligible: likely due to carbonate precipitating agent (higher purity possible with higher purity agent)

- S traces (<1%): likely due to sulfate precursors (additional washing steps might help improve)

- Al traces (<1%): likely due from ceramic boat. Future work could check with more stable boat (e.g. Pt foil) to determine if this is indeed source.



VSAMS PROJECT

Part 3

5

Formulation conditions:

Very thin electrodes : 2,5 to 6 mg/cm² – high error on the mass measurement of each electrode
 May lead to error in final capacity

Electrode's formulation:

	REF	V
AM	95,9	95,9
SP	2,1	2,3
PVDF	2,1	1,8

Cycling conditions:

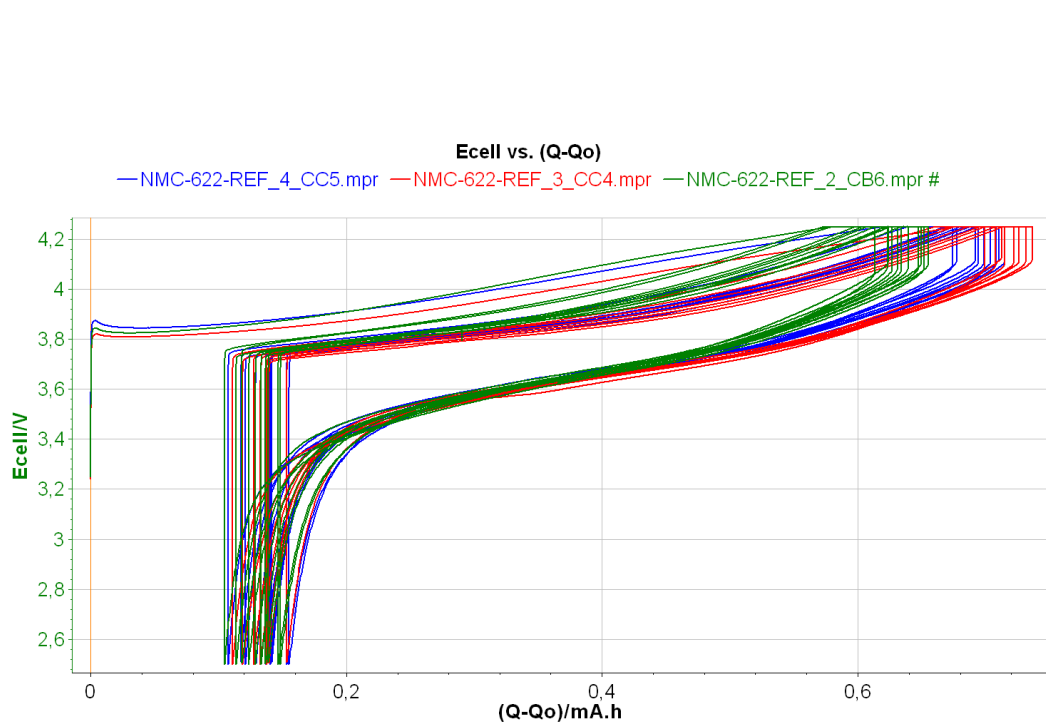
2,5 - 4,25 V

C/10 floating at discharge until C/20

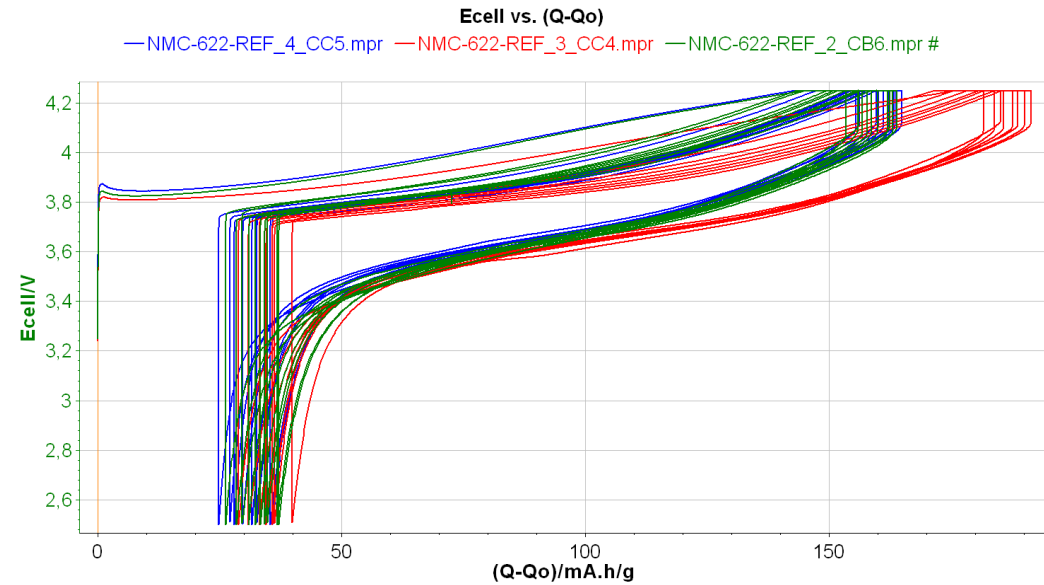
C = 166,2 mAh.g



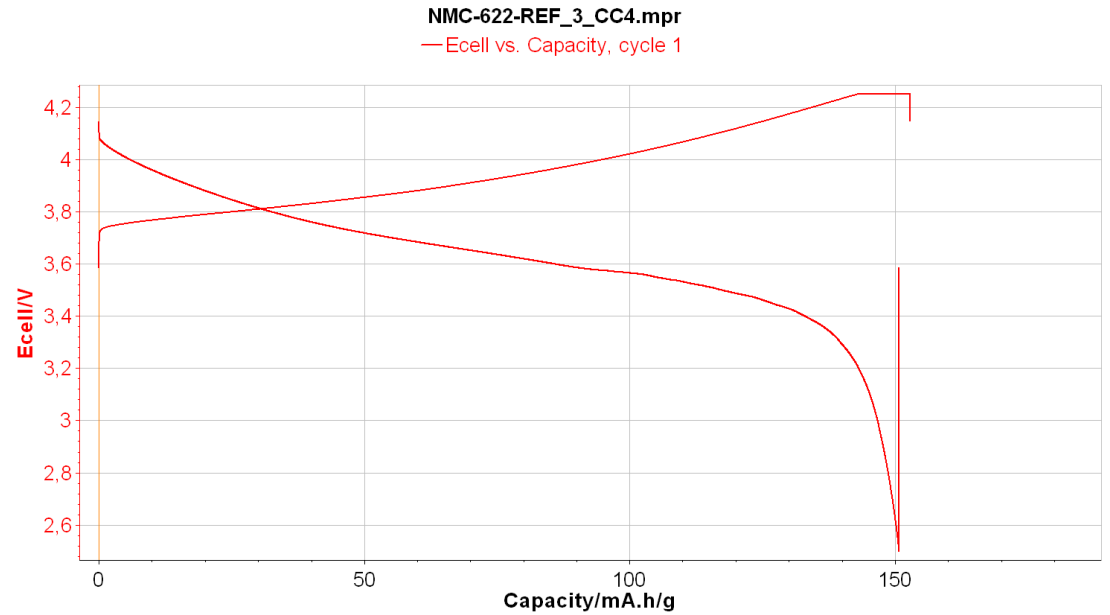
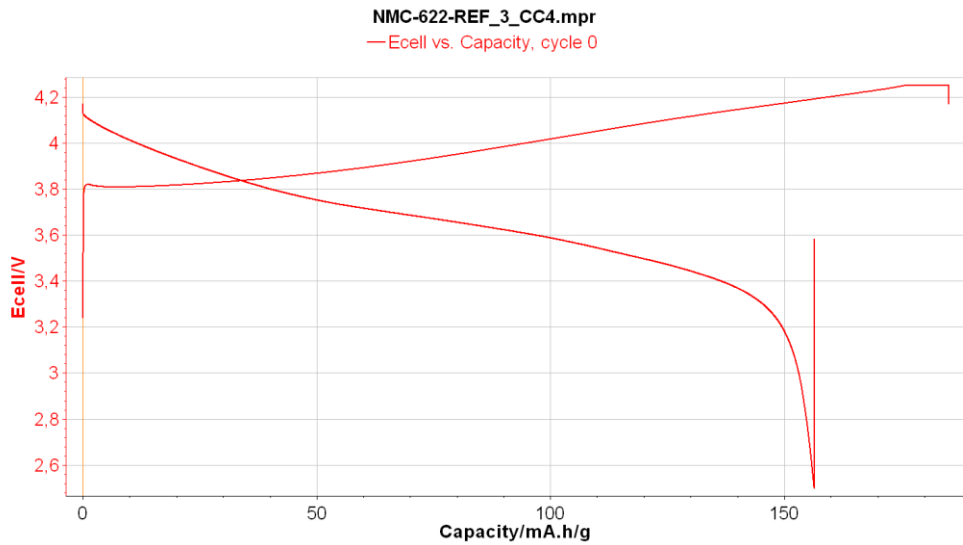
Cycling for Reference cell :



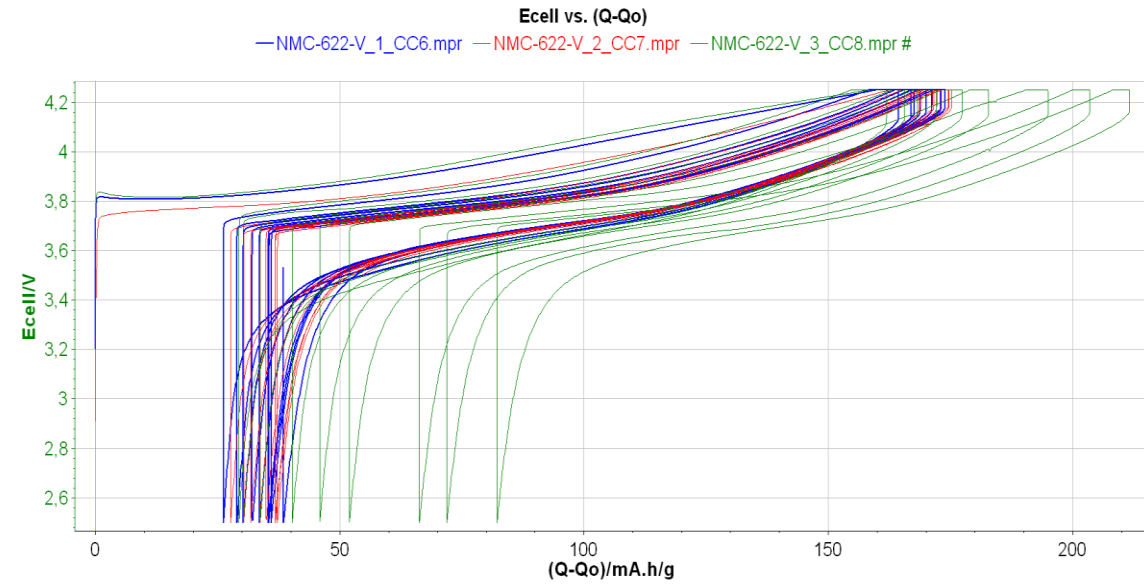
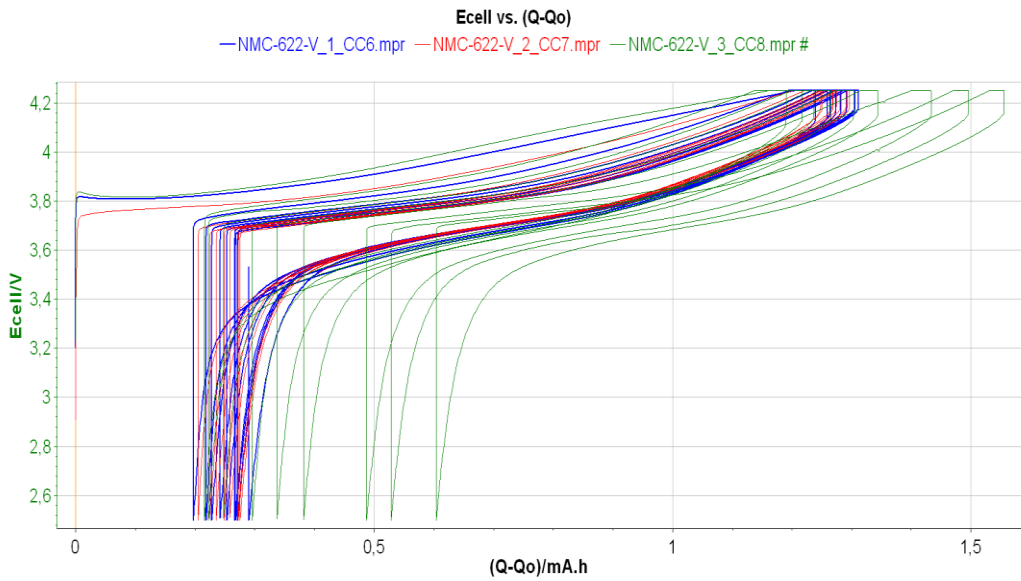
High polarization



Ecell for Reference Cell

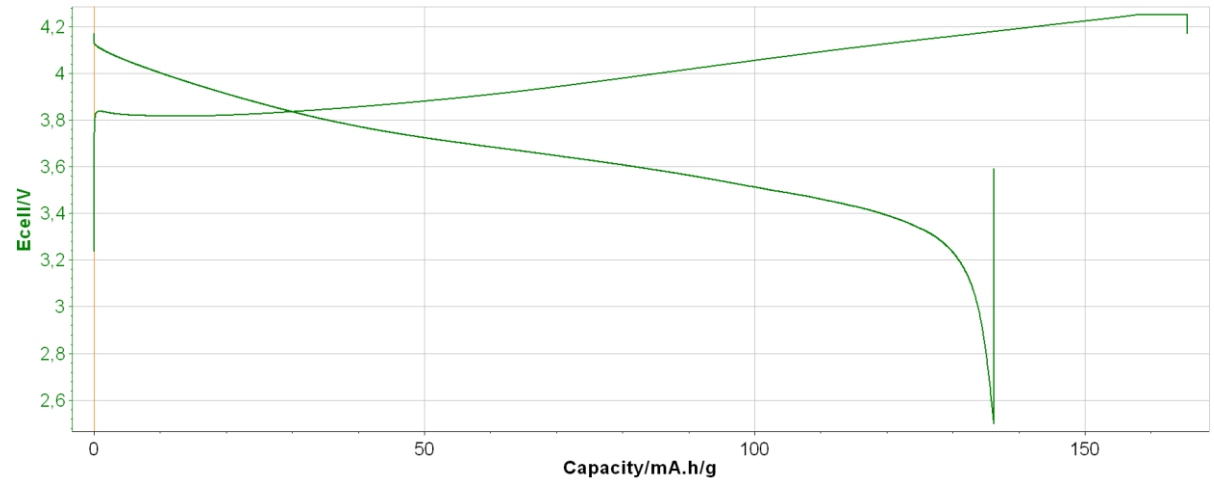


Cycling for V sample

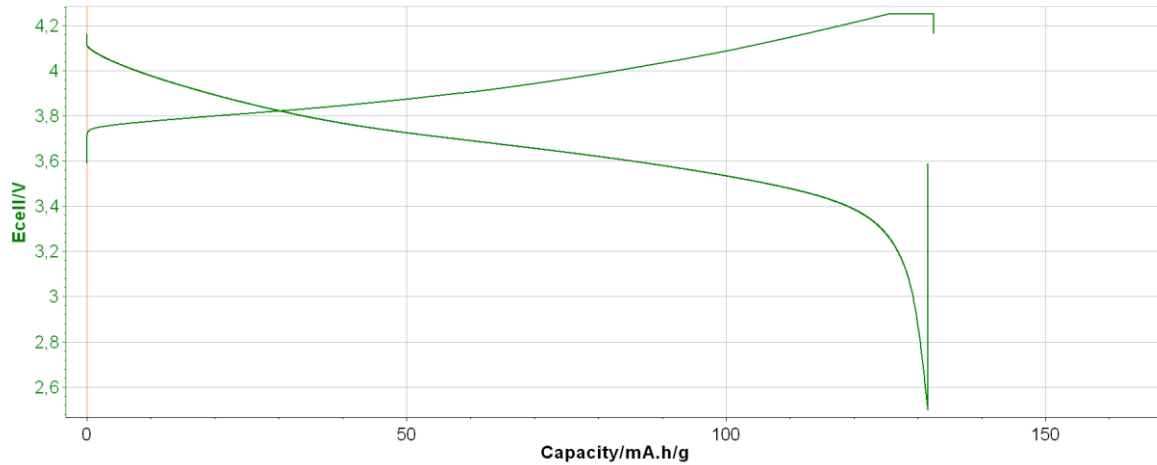


Ecell for V Sample

NMC-622-V_3_CC8.mpr
— Ecell vs. Capacity, cycle 0

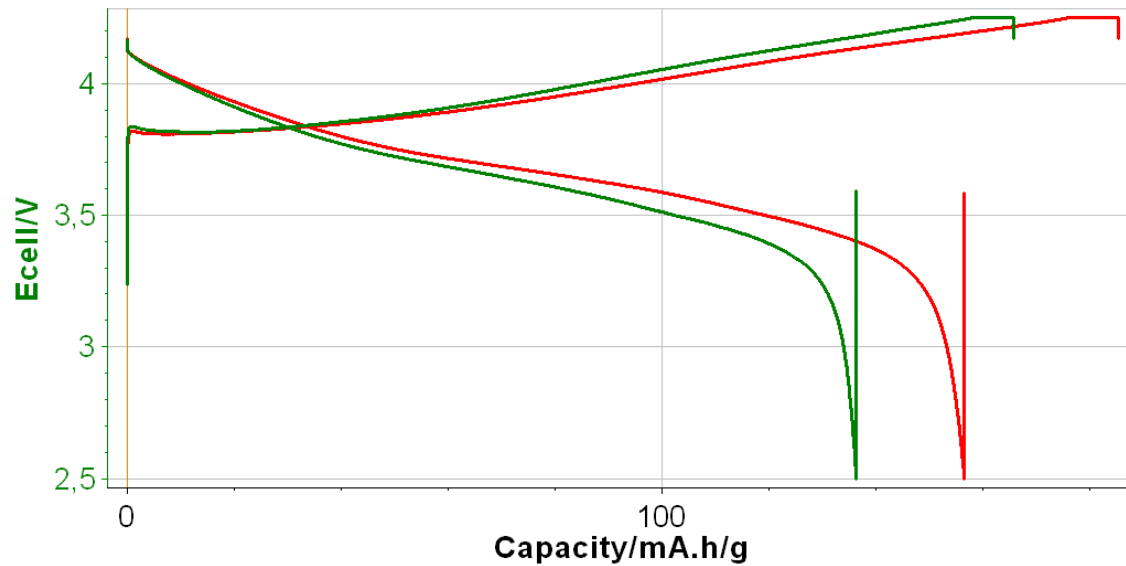


NMC-622-V_3_CC8.mpr
— Ecell vs. Capacity, cycle 1

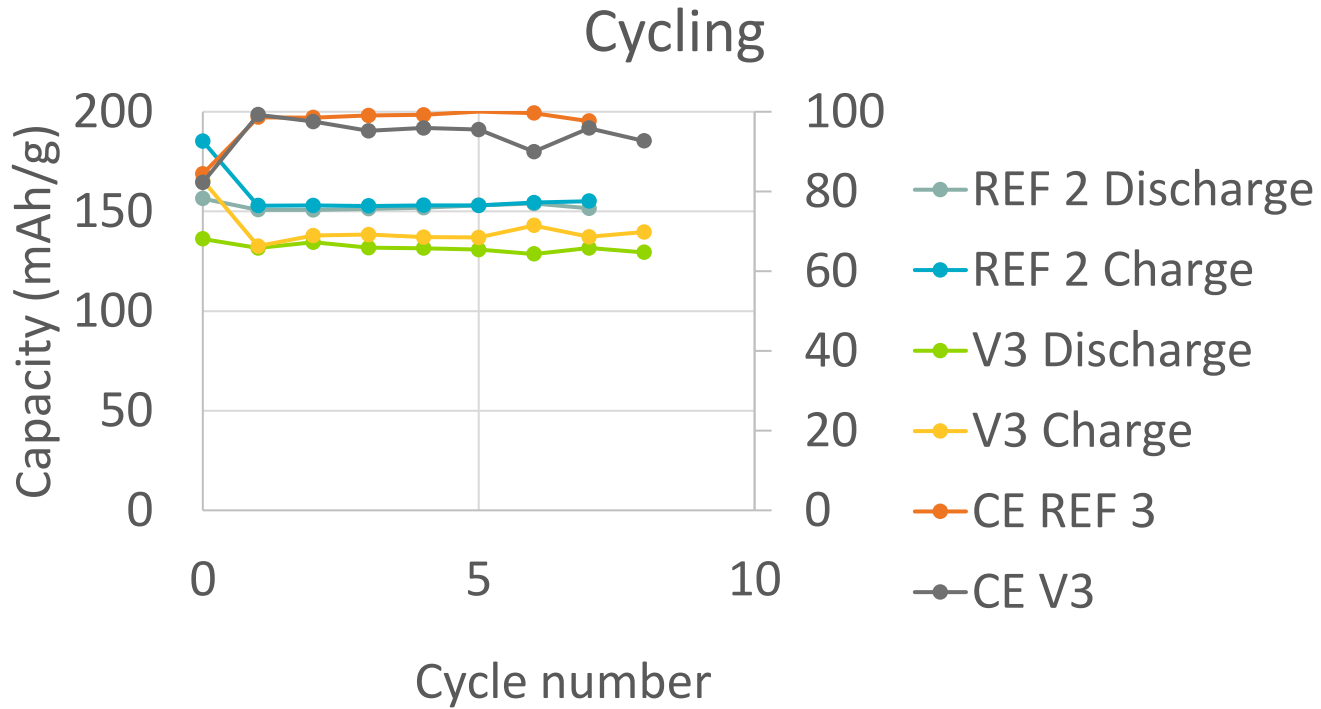


Comparison between Ref and V Sample

— NMC-622-V_3_CC8.mpr : Ecell vs. Capacity, cycle 0 #
— NMC-622-REF_3_CC4.mpr : Ecell vs. Capacity, cycle 0



Comparison between REF and V sample





VSAMS PROJECT Conclusion

6

Conclusion

Project conclusion:

Material MnSO_4 purity is **ok**

Material synthesis process of NMC 622 is **ok**

NMC reference and NMC V samples characterisation done with limited differences.

NMC reference and NMC V samples compared in coin cell :

- lower capacity for NMC V Sample
- **Same cycling behavior**

Difference in capacity could be due to lab NMC synthesis mass limitation. More tests should be done in more reproducible and « at-scale » process to validate MnSO_4 from GITA for NMC battery material. This option was not possible in the timing of VSAMS Project.

TRL3 achieved → could be continued in the following months to achieve TRL4





VSAMS PROJECT

Annex

6

Project follow-up options

- **OPTION A: Repeated Lab-scale NMC 622 batch synthesis**
 - ✓ ca. 1g product (sufficient for basic characterisation - e.g. purity, etc.)
 - ✓ Rapid and facile
 - ✓ Sufficient for basic half-cell characterisation
 - * Not necessarily representative of "at-scale" material



TRL3

- **Option B: Larger scale CSTR synthesis**
 - ✓ Basic material optimisation (e.g. purity, morphology, etc.)
 - ✓ Larger scale per batch (100s g already validated in system, for other materials)
 - ✓ Establish parameters for future work
 - * Increased time + cost



TRL4