
Nissan Leaf

Study of the cathode coating-drying manufacturing process by design of experiments

L.A. Román-Ramírez, G. Apachitei, M. Faraji Niri,
M. Lain, D. Widanalage and J. Marco
University of Warwick, WMG

International Battery Production Conference 2021

THE FARADAY INSTITUTION ELECTRODE MANUFACTURING NEXTRODE

OVERVIEW OF CELL MANUFACTURING PROCESS

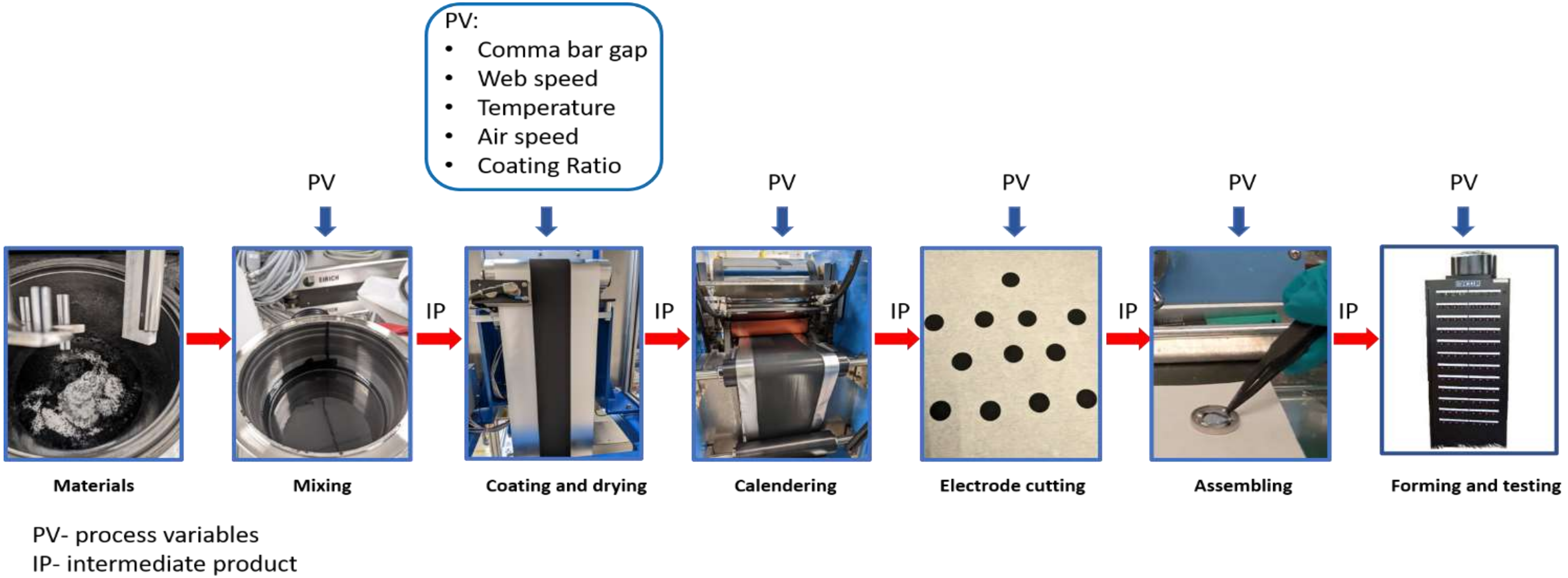

Fig. 1 Schematic diagram of the cell manufacturing process

- More than 600 variables involved. Turetskyy, A. et. Al., *Energy Technol.* **2020**, *8* (2), 1900136

- Design of experiments applied to coating and drying of NMC 622 cathode on pilot-line:
    - Correlations between the electrode properties and process variables obtained by multiple linear regression analysis
    - Correlations between half-coin cell performance and electrode physical properties (coating weight, porosity and thickness)

DESIGN OF EXPERIMENTS (DOE)

One variable at a time (OVAT)

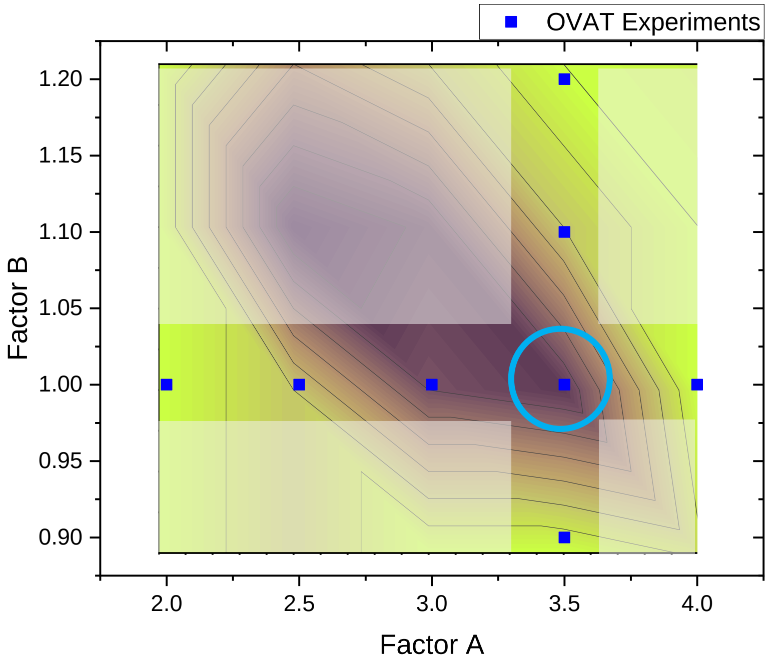

Fig. 1 Schematic representation of one variable at a time (OVAT) approach

Full factorial design of experiments

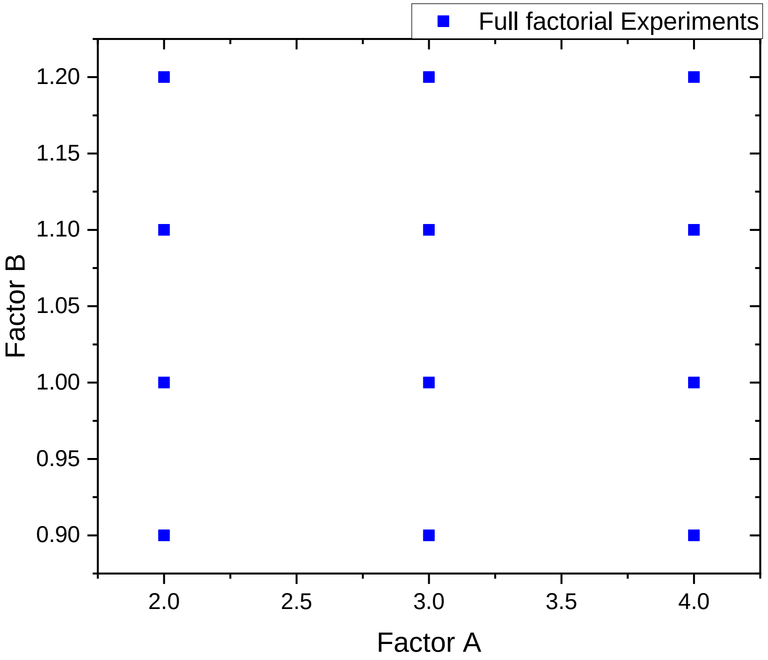

Fig. 2 Schematic representation of full factorial design of experiments

Screening design of experiments (DoE)

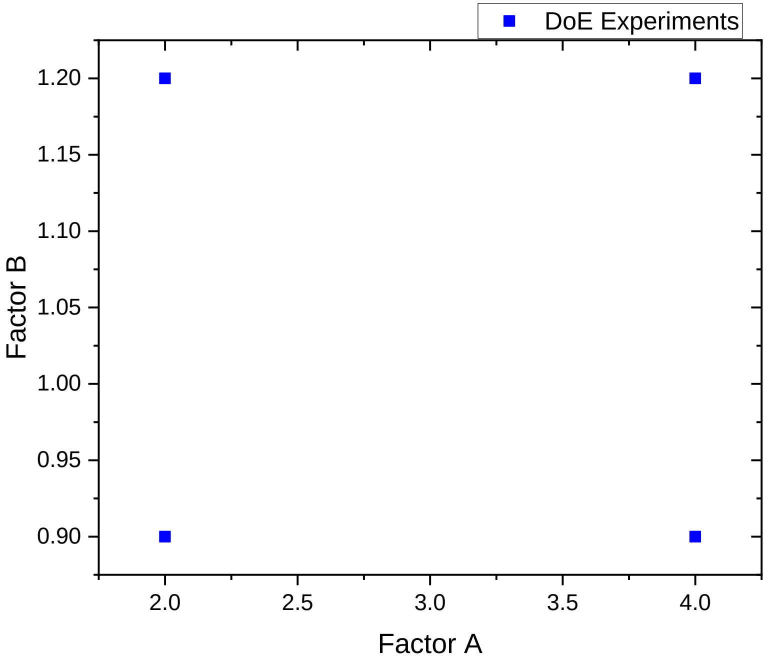

Fig. 3 Schematic representation of screening design of experiments

- DoE used to understand the effect of input variables (factors) on output variables (responses) and identify the main influences

ELECTRODE COATING PROCESS

Pilot- line coating equipment:

- Roll support dryer with effective drying length ~3.4 m
- Three zones with separate temperature and air settings (top and bottom nozzles)
- Real time coating weight reading (MeSys systems for wet and dry coating)

Fig. 1 Pilot-line equipment at WMG- coating and drying

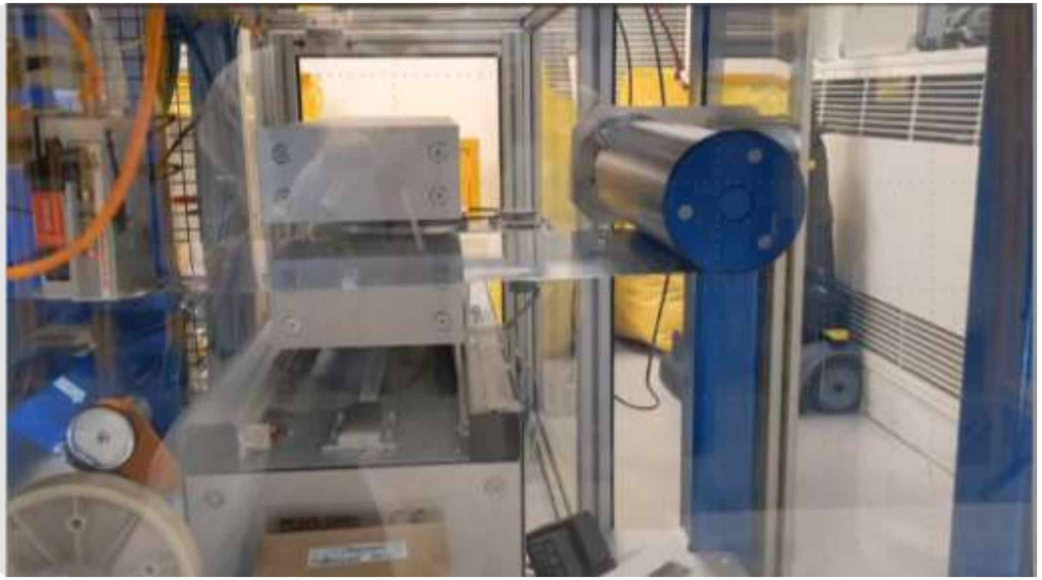

Fig. 2 MeSys setup for measuring coating weight in line

ELECTRODE RESPONSES

Measured:

- Thickness
- Mass
- Mass loadings dry and wet from MeSys systems- further processing in MATLAB
- Spatial autocorrelation and join counting (SAJC) Z-score
  - Scanning Electron Microscopy (SEM)
  - Energy Dispersive Spectroscopy (EDS) maps produced
  - Carbon and fluorine distribution
- Gravimetric and volumetric capacities of half-cells at : C/20, C/5, C/2, 1C, 2C, 5C and 10C rates

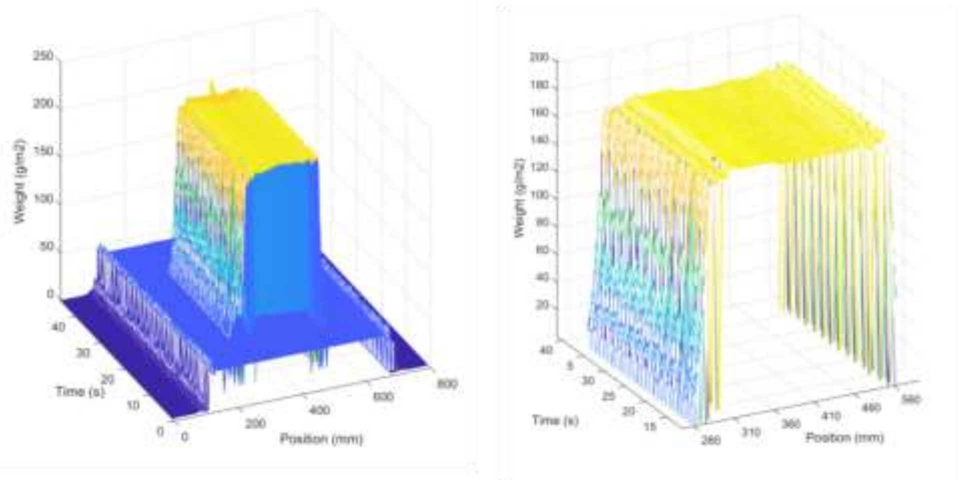

Fig. 1 Mass loading dry recorded data from MeSys System. Left: raw initial data, right: post-processed data

Calculated:

- Density
- Porosity
- First cycle loss of half-cells
- Rate performance at 5C:0.2C

Mona Faraji-Niri

DESIGN MATRIX (SET OF RUNS)

Screening design of experiments

				Design Matrix					
Factors	**No. of levels**	**Low**	**High**	**Experiment**	**Comma bar gap (µm)**	**Web speed (m/min)**	**Temperature (°C)**	**Air speed (m/s)**	**Coating ratio (%)**
Comma bar gap (µm)	2	80	140	1	140	0.5	85	5	150
Web speed (m/min)	2	0.5	1.5	2	80	0.5	85	15	150
Temperature[a] (°C)	2	85	110	3	80	1.5	110	5	150
Air speed (m/s)	2	5	15	4	140	0.5	110	5	110
Coating ratio (%)	2	110	150	5	80	1.5	85	5	110
				6	80	1.5	110	15	110
				7	140	1.5	110	5	150
				8	140	1.5	85	15	110
				9	140	1.5	85	15	150
				10	140	0.5	110	15	110
				11	80	0.5	85	5	110
				12	80	0.5	110	15	150

[a] Temperature of the first drying zone, the other two zones were held constant at 110 and 95 °C, respectively.

Table 1 Design matrix of experimental plan

STATISTICAL ANALYSIS

- Analysis of variance (ANOVA)
- Confidence level = 90% ($\alpha = 0.1$)
- Graphical response for:
    - normal plot of residuals: to check for normal distribution
    - Predicted vs actual: to identify potential outliers
    - Residual vs run: to rule out the presence of time trends
- Regression analysis
- Linear models of the form:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \varepsilon$$

where:
y = dependent variable (response)
x = independent variables (factors)
β = coefficients
i^{th} = factor
$\mathcal{E}$ = random error

- Goodness of fit determined by R^2

Luis Roman Ramirez

Results

RESULTS. OPERATING PARAMETERS AS THE INPUT FACTORS

- ANOVA performed for each of the responses
- Example of ANOVA result: mass loading of coin cell electrodes
- Model useful in predicting comma bar for obtaining target mass loading

ANOVA for Coating weight, cell

Full linear model

Source	Sum of Squares	Degrees of freedom	Mean Square	F-value	p-value
Model	29774.52	5	5954.9	45.87	0.0001
A-Comma bar gap	22575.82	1	22575.82	173.89	< 0.0001
B-Web speed	60.35	1	60.35	0.4648	0.5208
C-Temperature	131.27	1	131.27	1.01	0.3535
D-Air speed	47.48	1	47.48	0.3657	0.5675
E-Coating ratio	6959.6	1	6959.6	53.61	0.0003
Residual	778.99	6	129.83		
Corrected Total	30553.51	11			

Factors are coded.

Coefficients

Factor	Coefficient Estimate	Degrees of freedom	Standard Error	95% CI Low
Intercept	182.78	1	3.29	174.74
Comma bar gap	43.37	1	3.29	35.33
Web speed	2.24	1	3.29	-5.81
Temperature	-3.31	1	3.29	-11.36
Air speed	-1.99	1	3.29	-10.04
Coating ratio	24.08	1	3.29	16.03

Fit statistics

R^2	0.9745

Tab. 1 ANOVA for mass loading

MAIN OPERATING VARIABLES

- No statistically significant effect of 1st zone temperature on the studied responses, results supported by SAJC-Z score showing no correlation of carbon and fluorine distribution with input factors
- Comma bar gap, coating ratio and web speed seem to affect the electrode porosity
- Capacities at C rates higher than 2C are affected by the comma bar gap and coating ratio through the mass loading

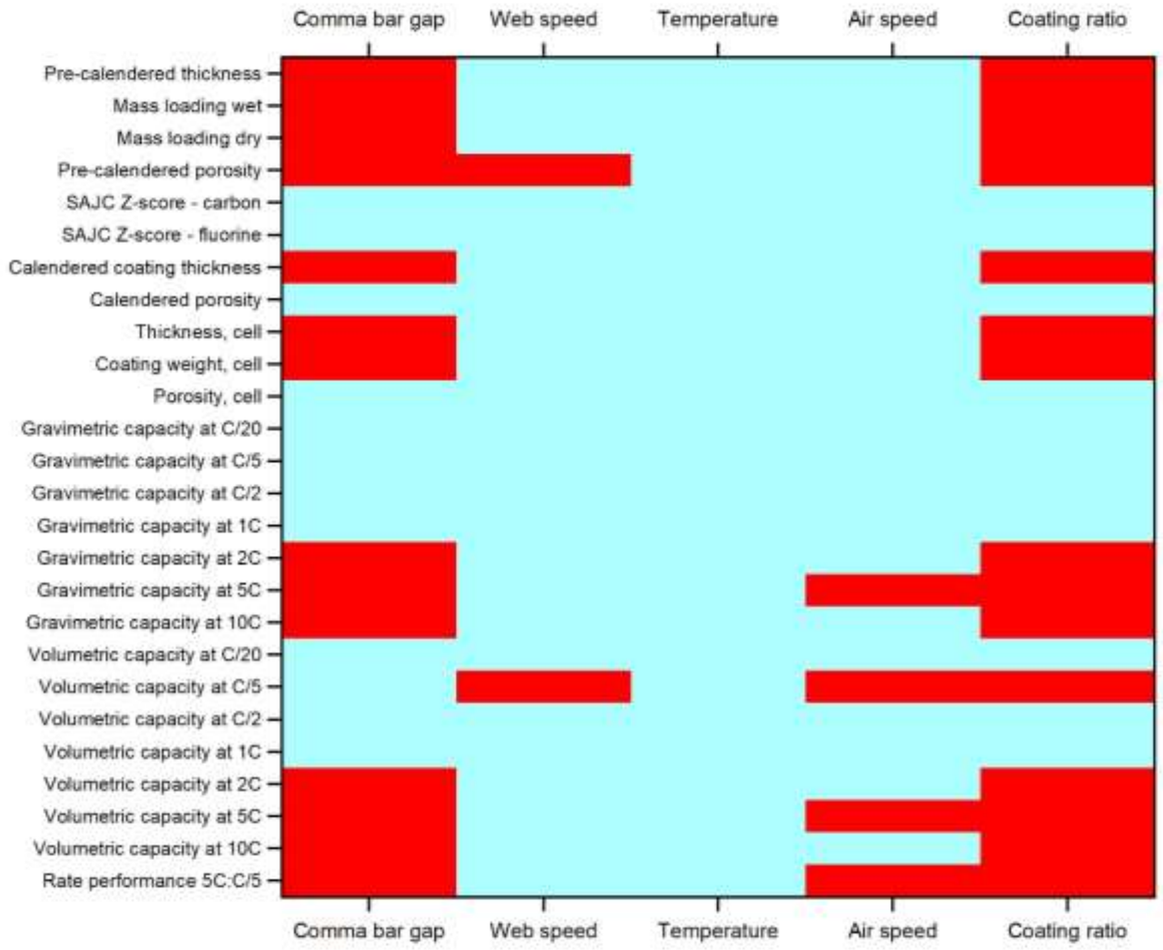

Fig. 1 Identified main operating variables (marked in red) according to ANOVA for each of the responses

MODEL COEFFICIENTS

Empirical model for the significant factors:

$$y^{\lambda} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i$$

	Response	λ	*Intercept*	*Comma bar gap*	*Web speed*	*Temperature*	*Air speed*	*Coating ratio*	R^2
Physical properties	Pre-calendered coating thickness	0	1.872	0.0868				0.0569	0.99
	Mass loading wet	-0.5	0.0626	-0.0073				-0.0040	0.98
	Mass loading dry	-0.5	0.0759	-0.0086				-0.0048	0.99
	Pre-calendered porosity	1	47.80	-1.400	-1.128			0.7650	0.84
	Calendered coating thickness	-0.5	0.1339	-0.0154				-0.0082	0.99
	Thickness, cell	-0.5	0.1329	-0.0159				-0.0075	0.99
	Coating weight, cell	-0.5	0.0761	-0.0091				-0.0048	0.99

- E.g. for mass loading dry:

$$y^{-0.5} = 0.0759 - 0.0086 * \text{comma bar gap} - 0.0048 * \text{coating ratio}$$

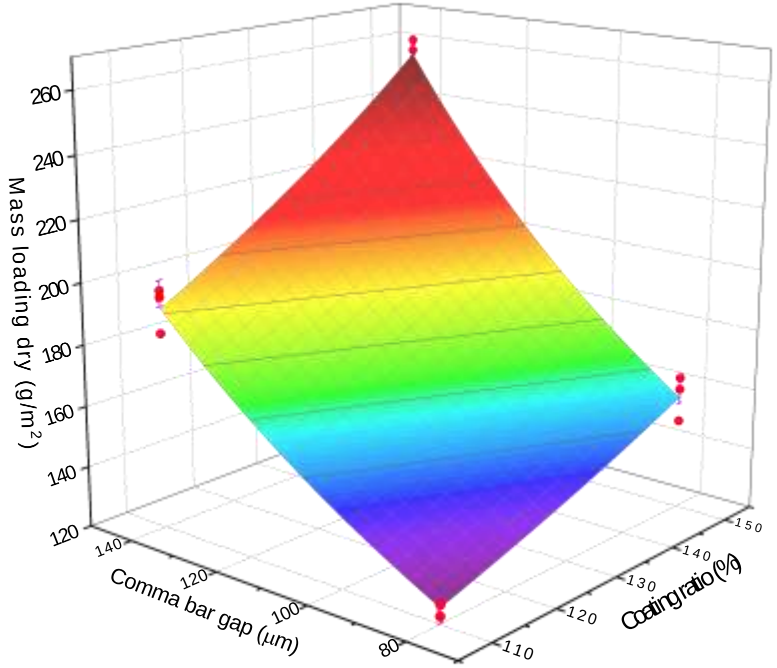

Fig. 1 Surface described by the empirical model for mass loading dry

RESULTS. CELL PHYSICAL PROPERTIES AS THE INPUT FACTORS

- ANOVA
- Only coating weight and porosity considered

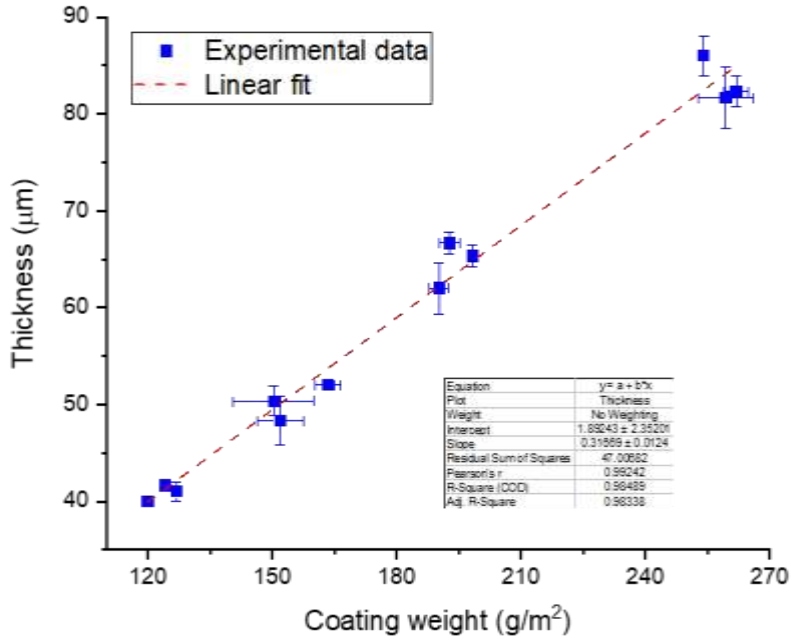

Fig. 1 Thickness vs coating weight plot and regression line

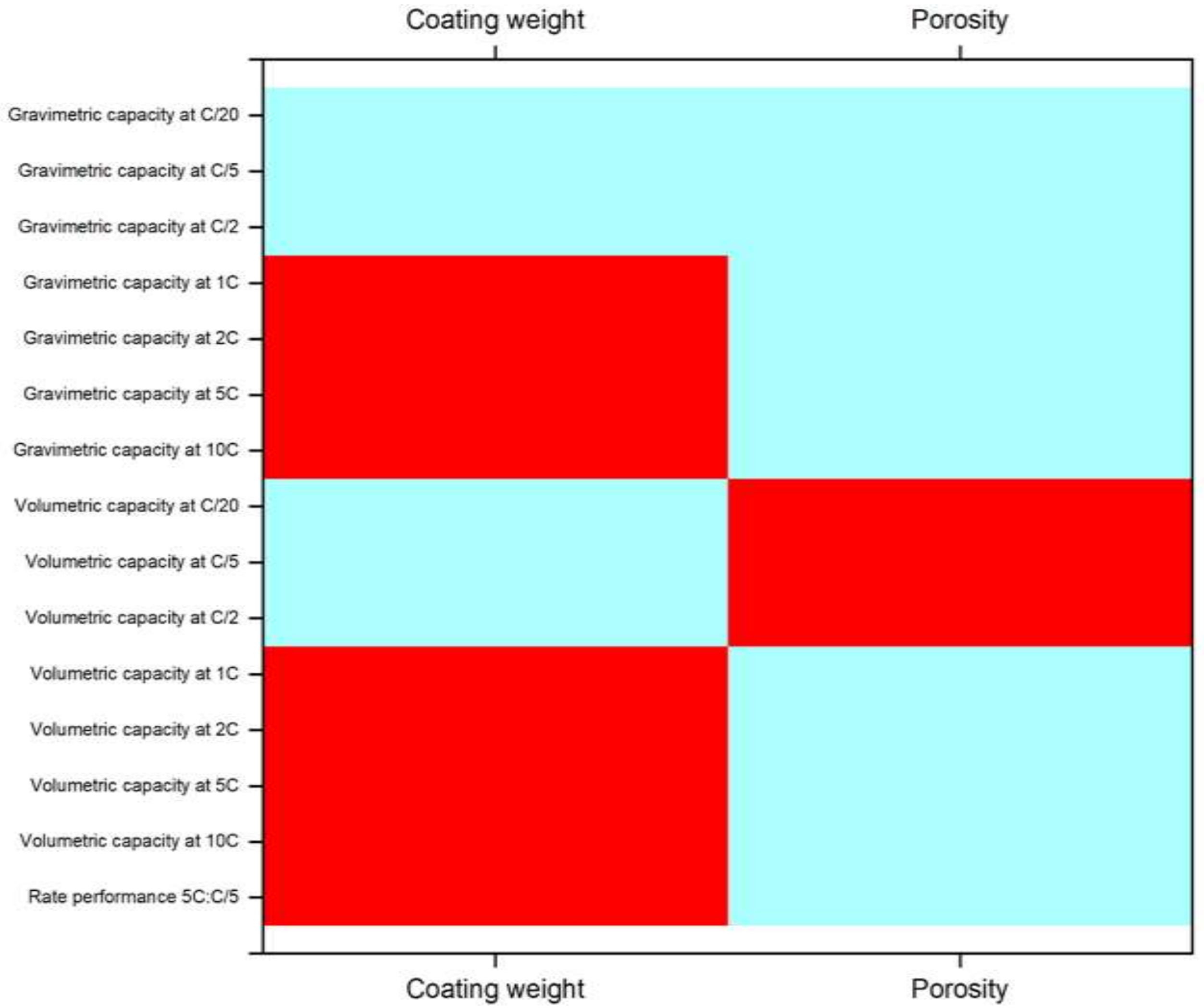

Fig. 2 Identified main cell physical properties (marked in red) according to ANOVA for each of the electrochemical responses

CONCLUSIONS

- DoE was used to identify the main operating variables of the coating-drying process at pilot plant scale of NMC cathodes
- Electrochemical performance was studied as a function of process variables and electrode physical properties
- Porosity proved to be important for the low C-rate volumetric capacities, while at high C rates, both gravimetric and volumetric capacities are affected mostly by mass loading
- No effects were observed from changing the drying conditions in the chosen ranges
- Simple empirical models were obtained to represent the relationship between the input and output variables
- Challenging in analysing and understanding processes

NEXTRODE PARTNER UNIVERSITIES/ ACKNOWLEDGEMENTS

The speaker would like to thank the Battery Scale-Up group at WMG, University of Warwick for all the support during this work.

WP5 OVERVIEW - TEAM

WP Leader

James Marco

Co Investigators

Dave Greenwood

Mark Copley

Dhammika Widanage

Lead engineer
Dr Giuseppe Elia

Lead engineer
Dr Mike Lain

Project engineer
Dr Geanina Apachitei

Project engineer
Daniela Emilia

Manufacturing and Cell Analysis

Manufacturing Electrode and Cell

Electrochemical Testing

Manufacturing

Research Fellow
Dr Luis Roman
Previous member

Research Fellow
Marc Hidalgo

Experimental design DoE Matrix creation

Parameter ID Sensitivity analysis

Experimental design

Senior Research Fellow
Dr Mona Faraji Niri

Data Mining, Curation and Formatting

Modelling, Classification, Feature Extraction, Sensitivity Analysis and Prediction

Modelling

Senior Research Fellow
Dr Kailong Liu
Associated researcher

Engagement with UKBIC

Manufacturing Quality, Process Capability Metrics

Thank you!

Geanina.Apachitei@warwick.ac.uk
www.nextrode.web.ox.ac.uk

Work accepted for publication in Journal of Power Sources- Understanding the effect of coating-drying operating variables on electrode physical and electrochemical properties of lithium-ion batteries

THE FARADAY INSTITUTION ELECTRODE MANUFACTURING NEXTRODE INDUSTRIAL STRATEGY UK Research and Innovation