

Electrophoretic deposition of LiFePO_4 and carbon black: A numerical study to explore longitudinal trends using Taguchi design

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ARTICLE INFO

Keywords:

Structural Battery
Electrophoretic Deposition
 LiFePO_4 coating
Numerical model
Structural Cathode

ABSTRACT

Developing Electrophoretic Deposition (EPD) for Composite Structural Batteries (CSBs) could revolutionise energy storage technology. CSBs offer an innovative solution by seamlessly integrating batteries into structures and effectively reducing weight and space constraints. Despite its successful implementation across various fields, EPD method still lacks comprehensive understanding of the underlying physical and chemical processes due to the number of variables involved. In this study the effects of key parameters associated with the process are investigated with a coupled FEM and analytical approach to find correlations with the deposition process. A Taguchi Design of Experiment with five parameters, namely voltage, concentration, relative weight ratio of LiFePO_4 – carbon black particles, length and perimeter of the electrodes is implemented to identify the correlations with mass deposited, thickness of the coating and yield rate when LiFePO_4 and Carbon Black particles in ethanol suspension are used. In order to capture the variation over time, each parameter is studied at six different time of deposition. A concentration that optimises yield rate resulting in thickness and mass deposition is identified. The resistivity of the suspension dictates the yield rate dynamics, allowing it to be designed within a specific range to meet requirements of different applications.

1. Introduction

The manufacturing of structural batteries typically involves a configuration comprising a sealed pouch bag containing carbon fibres (CF) as the anode, a coated aluminium foil as the cathode, and a bi-continuous polymer electrolyte. Feasible manufacturing processes for the deposition of the active material can be categorised into two main techniques: direct and indirect methods. Direct methods focus on creating cathode materials directly on the structural support. Indirect methods primarily involve depositing cathode materials onto structural supports. Among these methods, electrophoretic deposition (EPD) is an economical technique which uses water or aqueous suspensions and an electric field to deposit charged particles onto a substrate. While these solvents provide advantages like high solid loadings and environmental benefits, they can trigger undesired electrochemical reactions at electrode surfaces. Consequently, organic media are becoming more favoured to mitigate these issues.

EPD emerges as a highly promising manufacturing method for

composite structural battery cathodes, overcoming the challenges associated with integrating components within the main structure.

The optimisation of EPD revolves around achieving desired outcomes in terms of uniformity of deposit, density/packing, thickness, and adhesion to the substrate. This optimisation aims at stabilising the particle dispersion, a condition influenced by several parameters including particle size, value of zeta potential, fluid dielectric constant, viscosity and conductivity of the dispersion [1]. Collectively, these parameters govern the dynamics of charged particles, ensuring their uniform dispersion, charge repulsion, and responsiveness to the applied electric field. These parameters dictate the forces that operate among the particles, and between the particles and the surrounding fluid, preserving a thermodynamically metastable state within the solution [2,3].

The mechanisms associated with the deposition were first studied by Hamaker in 1939 [4]. His study included the EPD of different suspensions, mainly using organic solvents such as acetone, ethanol, and methanol [4]. Hirata et al. [5] derived a new linear equation from Faraday's law of electrophoresis from which, considering a fixed

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<https://doi.org/10.1016/j.matdes.2024.113446>

Received 22 July 2024; Received in revised form 29 October 2024; Accepted 7 November 2024

Available online 9 November 2024

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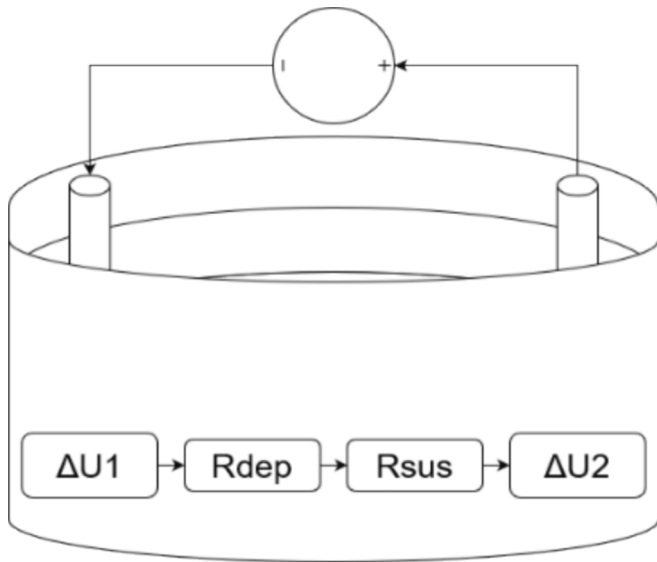


Fig. 1. EPD cell overall potential drop (Re. adapted from [11])

Table 1

Experimental values of Zeta Potential, Electrophoretic Mobility and Electrical Resistivity of suspension at different particle concentration (C) levels and of pure ethanol.

Relative Weight Ratio LiFePO ₄ /CB	30/70	70/30	85/15
Zeta Potential (mV)	-23.575 ± 1.068	-24.508 ± 1.792	-26.433 ± 0.915
Electrophoretic Mobility (cm ² /Vs) × 10 ⁻⁵	4.612 ± 0.208	5.165 ± 0.351	5.599 ± 0.178
Resistivity (Ω cm) at C = 0.005 g/cm ³	1703	22,915	26,353
Resistivity (Ω cm) at C = 0.0002 g/cm ³	37,875	49,525	36,666
Resistivity (Ω cm) at C = 0.00005 g/cm ³	68,893	42,953	79,937
Resistivity (Ω cm) at C = 0.0000125 g/cm ³	69,006	101,265	94,287
Resistivity (Ω cm) at C = 0.000003 g/cm ³	N/A	156,909	89,846
Resistivity (Ω cm) of Ethanol	206,228	206,228	206,228

experimental setup, one can conclude that the weight of the deposit is directly proportional to the concentration of solids in suspension, the time of deposition and the applied electric field [11]. The problem with these models is that the deposited weight is in a linear relationship with time, and therefore, assumes that the other parameters remain constant throughout the process. This is verified only for short periods of time, or for constant current and constant concentration [1,6,7].

When EPD is performed at constant-voltage and variable-concentration conditions current drops, due to the increased resistance of the deposited material compared to the bulk of the dispersion, are observed. In literature, several EPD experiments with constant voltage and variable concentration conditions have been reported.

Zhang et al. [8], derived an equation to estimate the yield based on the mass conservation law. This was validated performing EPD of SiC whiskers and t-ZrO₂ particles in a mixed solution of methanol and 2-propanol. The electric field during the deposition process was monitored, observing a decrease in the values of current measured during the process. In the same experiments, it was demonstrated the linear correlation between the electric field drop and the thickness of the deposited material.

Sarkar & Nicholson [6] studied the kinetics of the EPD process

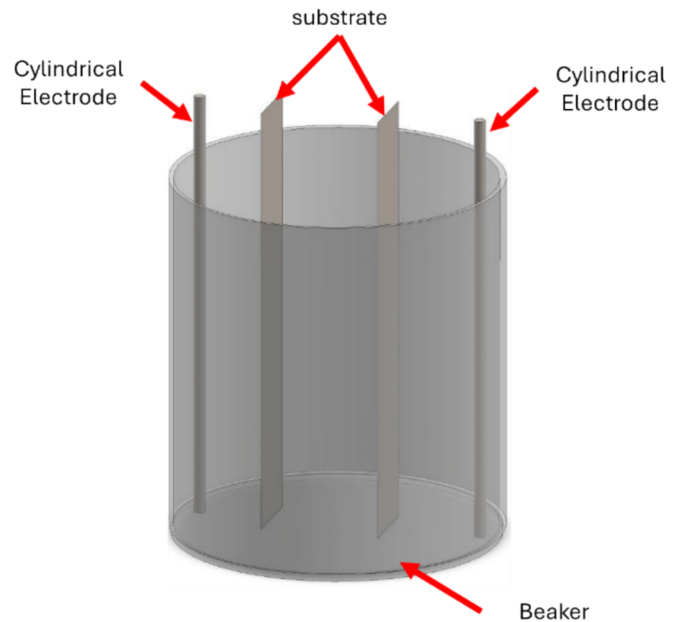


Fig. 3. 3D model of Geometry setup.

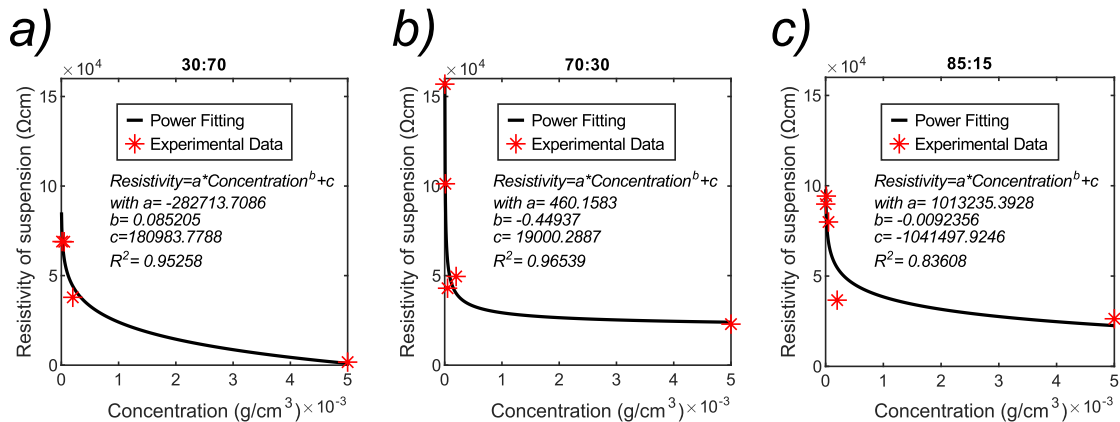


Fig. 2. Resistivity-Concentration plots. a) Data and fitting for LiFePO₄/CB = 30/70. b) Data and fitting for LiFePO₄/CB = 70/30. c) Data and fitting for LiFePO₄/CB = 85/15.

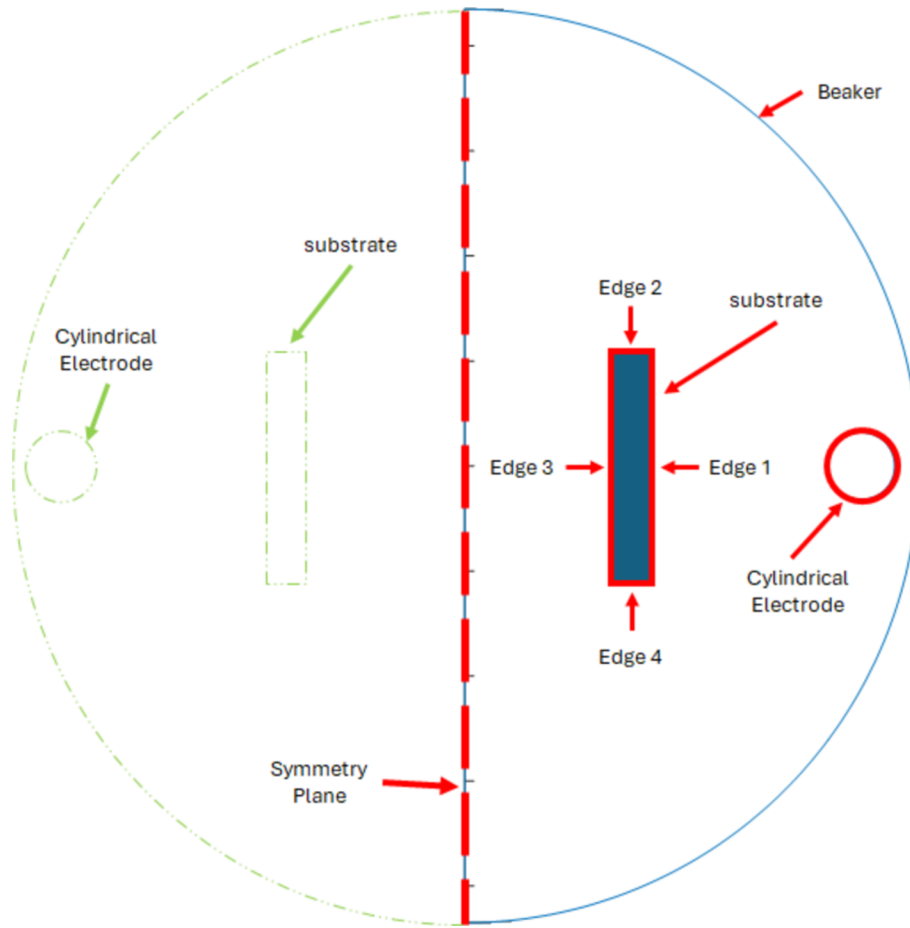


Fig. 4. Top view of the beaker with the electrodes and the substrates highlighting the domain used for the simulation on the right.

assuming constant-current and constant-voltage conditions. Biesheuvel and Verweij [9], combining Laplace equation with continuity in the suspension phase, provided a correction of the Hamaker's equation introducing concentration as a function of time. González-Cuenca et al. [10] derived an equation for constant-voltage EPD in a stirred suspension assuming a net zero charge in the system. The rate of cast growth is correlated with particle mass balance, Laplace equation, and the effective permittivity of the particle-liquid system. They [10] also criticised the conclusions drawn by other authors (e.g., [6,8]) who have used the increased resistance of the deposit as a justification for the electric field drops. Instead, the relative permittivity of deposit and suspension is assumed to be the root cause, in contrast with the work of other authors [6,17–20]. This observation highlights the ongoing challenge of achieving a robust understanding of the chemical and physical processes underlying EPD.

Anné et al. [11], using an equivalent electric circuit (Fig. 1), derived an equation for EPD based on Biesheuvel and Verweij's equation [9] that included the drop of the electric field due to increasing resistance of the deposit. They validated the equation experimentally through constant-voltage EPD at 300V of Al_2O_3 in methylethylketone with n-butylamine and ethanol.

The overall potential drop during EPD was described with Eq. (1).

$$U = \Delta U_1 + (d_1 r_{dep} + (d - d_1) r_{susp}) I + \Delta U_2 \quad (1)$$

Where ΔU_1 and ΔU_2 are the potential drops across the electrodes, while r_{dep} and r_{susp} are the resistance of the deposit and suspension respectively, that can be calculated knowing the resistivity and the thickness of the deposit and the interelectrode distance d_1 and d respectively.

Ferrari and Moreno in 2006 [12,13] further developed the model

proposed by Anné et al. to describe a linear relationship between variation of resistivity and concentration proposing the linear relationship in Eq. (2).

$$\rho = \rho_\infty - (\rho_\infty - \rho_0) \frac{c}{c_0} \quad (2)$$

Where ρ_0 is the initial resistivity of the suspension and ρ_∞ is the resistivity of the suspension when all the material is deposited ($c=0$). From Eq. (2) the EPD yield is derived (Eq. (3)).

$$w(t) = w_0 \left(1 - \frac{1}{1 + \frac{\rho_0}{\rho_\infty} \left(e^{\frac{I \rho_\infty \mu_e C_0 t}{w_0}} - 1 \right)} \right) \quad (3)$$

When $\rho_\infty = \rho = \text{constant}$ Eq. (3) becomes Sarkar and Nicholson's model, and it becomes Hamaker's equation when $t \ll \frac{I \rho_\infty \mu_e C_0}{w_0}$.

In 2019, A. Lavrov [14] modelled EPD via Discrete Element Method for small Debye length systems. Instead of relying on one of the different empirical formulas available in literature, the author built the model by analysing all the different forces acting on particles in an EPD system. The author includes the following forces in his model:

- Hydrodynamic forces,
- Electric forces due to the applied electric field,
- Attractive van der Waals interparticle forces,
- Repulsive interparticle forces due to the electrical double layer,
- Gravity and buoyancy forces.

More recently, Salazar de Troya et al. [15] studied the EPD of

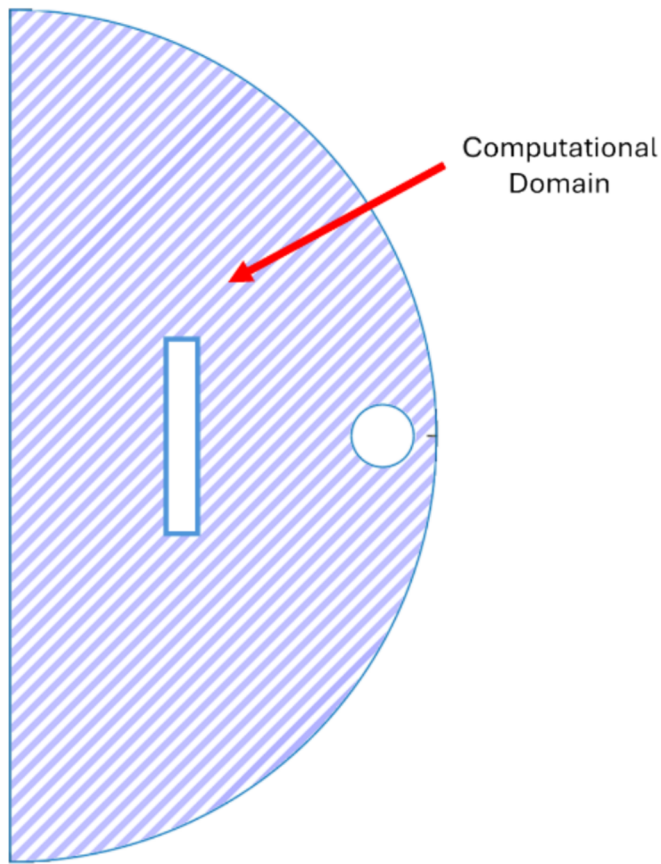


Fig. 5. Domain used for the simulation.

functionally graded materials using Finite Element Method. The work is based on the hypothesis that by actively shifting from an EPD bath to another, the graded material is deposited.

Different research studies have highlighted the significance of employing Design of Experiments (DoE) methodologies to investigate the relevance and impact of various parameters on electrophoretic deposition processes. In a study conducted by Datta S. [16], a 2^3 factorial design DoE was employed for the optimisation of glass–ceramic coating on a metal substrate via EPD in aqueous suspension. The

parameters scrutinised were concentration of solids in suspension, current and time. The deposition rate was linked to the selected parameters via Hamaker's equation and analysed via linear regression analysis. Similarly, Abbas R.A. et al. [17], used a L9 Taguchi orthogonal array to assess the influence of applied voltage, deposition time, and suspension concentration on thickness of yttria stabilised zirconia coatings deposited through EPD. The microstructure of the coatings was analysed for different combinations of the parameters to find the optimum balance between thickness and morphology. Mohanty G. et al. [18], employed a 2^4 full factorial DoE to analyse the effects of concentration, electrode separation, voltage, and time on the yield deposited. Steel substrates were coated with alumina in a suspension of isopropanol via constant voltage EPD. The concentration of the suspension emerged as the dominant factor influencing the yield of the deposition. Moreover, Taguchi design method has been used to study different manufacturing methods. Sivapragash M. et al. [19] employed an L18 Taguchi orthogonal array to examine the effects of three parameters for Physical Vapour Deposition (PVD) in order to optimise the micro hardness and minimise the wear rate of a ZrN coating on AZ91D magnesium alloy. Through regression analysis and Analysis of Variance (ANOVA), the optimal configuration was identified and experimentally validated. Amir B. et al. [20] studied the effect of laser powder bed fusion, an additive manufacturing technique, on the dynamic properties of an AlSi10Mg alloy. An L27 Taguchi orthogonal array was employed to correlate the effects of six parameters to six results. Regression analysis and ANOVA were used to investigate the response.

This work investigates, for the first time, the effects of various electrochemical and geometrical parameters on the performance of the EPD process. Using MATLAB's Electromagnetic Partial Differential Equation Toolbox in conjunction with EPD equations, this study models the deposition process. The correlations developed here enable highly controlled and uniform deposition of active materials onto electrode

Table 2
Taguchi Design of Experiment parameters, model name and levels.

Model name	Levels		
	1	2	3
V_{in} (V)	30	70	120
%wt	30	70	85
P (cm)	1	2	3
L_d (cm)	0.996	1.996	2.996
C (g/cm ³)	0.0005	0.00275	0.005

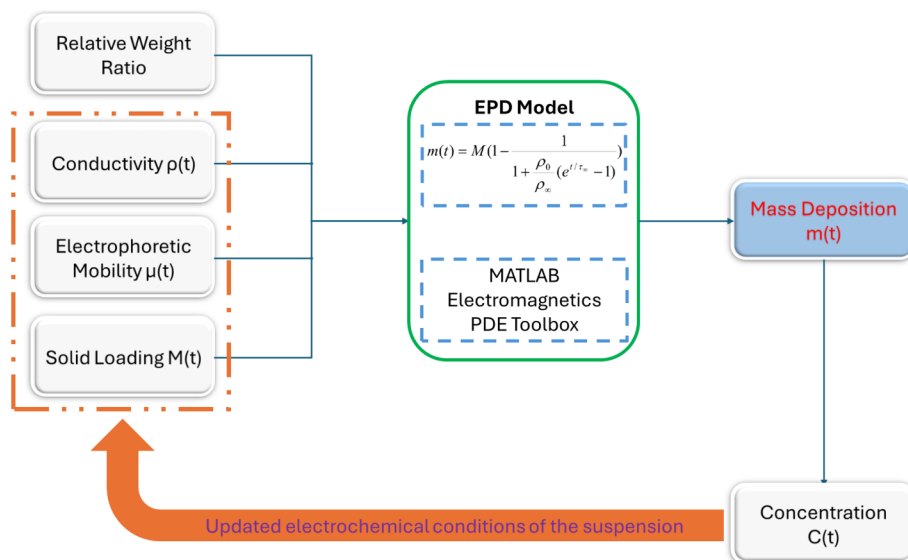


Fig. 6. Block scheme of MATLAB numerical model.

Table 3

Taguchi L27 orthogonal array.

Run	V_{in} (V)	%wt (%)	P (cm)	L_d (cm)	C (g/cm ³)
1	30	30	1	0.996	0.00050
2	30	30	1	0.996	0.00275
3	30	30	1	0.996	0.00500
4	30	70	2	1.996	0.00050
5	30	70	2	1.996	0.00275
6	30	70	2	1.996	0.00500
7	30	85	3	2.996	0.00050
8	30	85	3	2.996	0.00275
9	30	85	3	2.996	0.00500
10	70	30	2	2.996	0.00050
11	70	30	2	2.996	0.00275
12	70	30	2	2.996	0.00500
13	70	70	3	0.996	0.00050
14	70	70	3	0.996	0.00275
15	70	70	3	0.996	0.00500
16	70	85	1	1.996	0.00050
17	70	85	1	1.996	0.00275
18	70	85	1	1.996	0.00500
19	120	30	3	1.996	0.00050
20	120	30	3	1.996	0.00275
21	120	30	3	1.996	0.00500
22	120	70	1	2.996	0.00050
23	120	70	1	2.996	0.00275
24	120	70	1	2.996	0.00500
25	120	85	2	0.996	0.00050
26	120	85	2	0.996	0.00275
27	120	85	2	0.996	0.00500

substrates with complex geometries. The results produced in this study are crucial for selecting optimal parameters for active material deposition with EPD.

Moreover, the electrochemical performance of EPD-processed electrodes is influenced by the porosity and composition of the deposited layer, which are directly linked to the deposition current and rate (as faster deposition may lead to increased porosity). This work provides correlations to guide deposition conditions, thereby controlling deposition rate and ultimately electrode morphology. These insights are essential for creating high-quality electrodes in lithium-ion and other advanced batteries, enhancing charge/discharge efficiency and cycle life.

2. Materials and methods

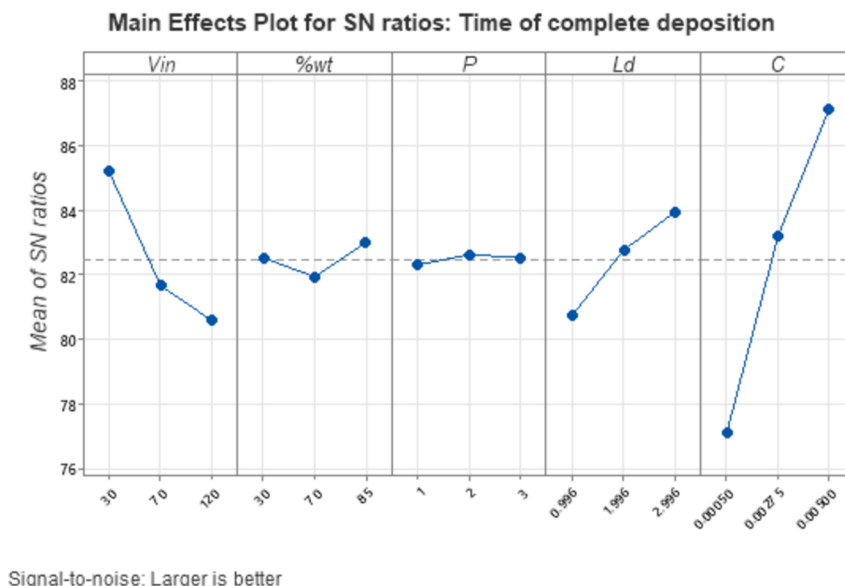
2.1. Experimental identification of zeta potential and electrical conductivity

The numerical model adopted to simulate the EPD relies on the identification of zeta potential, electrophoretic mobility and electrical conductivity for the system composed by the solvent and the particles. For this reason, samples for zeta potential measurements were prepared by dispersing 5 mg of particles in 25 mL of ethanol. The samples were ultrasonicated for 20 min and then 760 μ L of dispersion were injected into the capillary zeta cell for the zeta potential measurements. For each of the three relative weight ratios between LiFePO₄ and Carbon Black, a minimum of 6 different measurements were performed. In literature the use of dispersants including poly(4-styrene sulfonic acid) (PSSA), poly(ammonium acrylate) (PAA-NH₄) and poly(acrylic acid-co-maleic acid) (PAMA) as well as the using of carbon coating of LiFePO₄ particles has been studied [21,22] to describe the effect on the value of zeta potential. It is well reported that the zeta potential can significantly increase as the thickness of the carbon coating layer increases whilst the use of dispersants can become detrimental over certain concentration. For the purpose of this study, the effectiveness of the approach is not influenced by the use of any additive in the solution as the only modification required would be to perform the measurements of the zeta potential.

The conductivity of the suspension with different concentrations of LiFePO₄ and carbon black has been assessed using a standard three-electrode cell comprising a gold foil working electrode, a platinum coil counter electrode, and a reversible hydrogen electrode as the reference electrode.

The values used in the numerical model for both zeta potential, electrophoretic mobility, and resistivity at different concentrations are shown in Table 1.

The materials used for the characterisation are Lithium Iron (II) Phosphate (LiFePO₄) powder in <5 μ m particle size is supplied from Sigma Aldrich (Gillingham, UK). Carbon Black (CB), 100% compressed, in particles, is purchased from Fisher Scientific (Loughborough, UK). Particles are immersed in 95% pure ethanol (Sigma Aldrich, Gillingham, UK). The materials are used as received from the supplier. Zeta potential and electrophoretic mobility of the particles in suspension are determined using a Zetasizer Nano ZS ZEN3600 (Malvern Instruments Ltd., Malvern, UK) across varying particle concentrations and weight ratios

**Fig. 7.** S/N ratios main effect plot for Time of complete deposition.

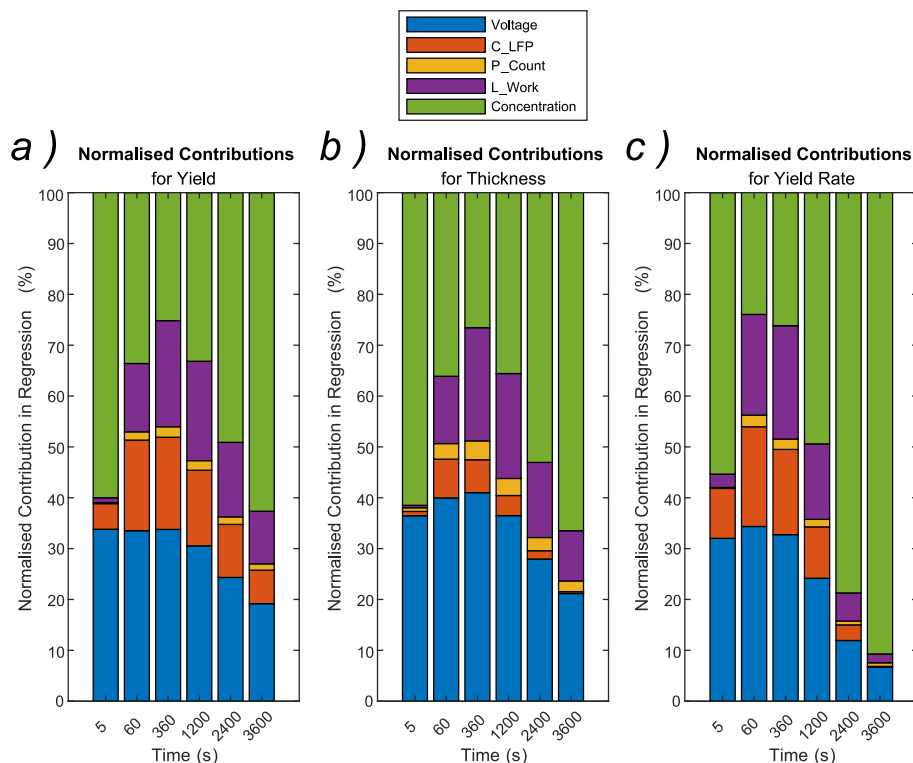


Fig. 8. Stacked bar charts for normalised contribution in regression against analysed timesteps. a) Normalised Contribution for Yield. b) Normalised Contribution for Thickness. c) Normalised Contribution for Yield Rate.

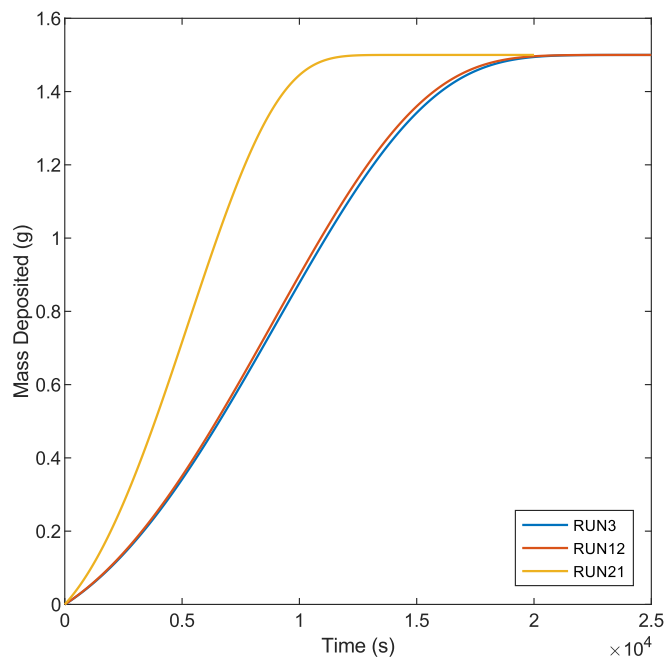


Fig. 9. Mass-time deposition curves for runs 3,12,21.

between LiFePO₄ and carbon black.

The resistivity of the solutions was measured at different values of particles concentration in solutions and grouped for different LiFePO₄/CB ratios. Fig. 2 shows different trends observed for the resistivity of the suspension as a function of the concentration. The experimental data-point have been fitted with a power law, instead of the linear correlation suggested by Ferrari and Moreno [13], and the functions have been used

in the numerical model implemented in MATLAB to describe the variation in concentration during the deposition process. The weight ratio for LiFePO₄/CB ranges from 30/70 to 85/15 in order to have a very wide range to identify the effects on the evolution of current and rate of deposition and also identify the optimum conditions for the EPD.

2.2. Implementation of the EPD model in MATLAB

The numerical model is represented by a cylindrical beaker having a capacity of 300 mL, inner diameter of 87 mm and height of 132 mm. Two cylindrical electrodes having diameter of 3 mm and length of 200 mm are made of stainless steel and positioned at a distance of 20 mm from the flat 20 μm aluminium substrate (Fig. 3). It is assumed that the distribution of particles in the suspension is uniform, and the electrical properties are the same in every point of the suspension.

Assuming that the electric field is constant throughout the depth of the beaker and there is no interaction between the layers at different depths, a 2D section of the beaker is modelled (Fig. 4) and because of the symmetry in the geometry and electric field, half of the section is considered. The effects associated with the variation in temperature that will produce change in viscosity and electrical conductivity [23] are not considered and the simulations are assumed at constant ambient temperature. However, the temperature increase due to Joule effect can be implemented in this model through the instantaneous values of resistivity and current at every timestep. The dependant parameters, including electrophoretic mobility and resistivity, will need to be defined as a function of temperature and the validity of the numerical model is not affected.

The numerical model is implemented in MATLAB release R2022b, version 9.13.0 using the PDE Electromagnetics Toolbox to estimate the electric field, electric potential, and the current density by means of the Laplace Eq. (4) [9,10]:

$$-\nabla \cdot (\sigma \nabla V) = 0 \quad (4)$$

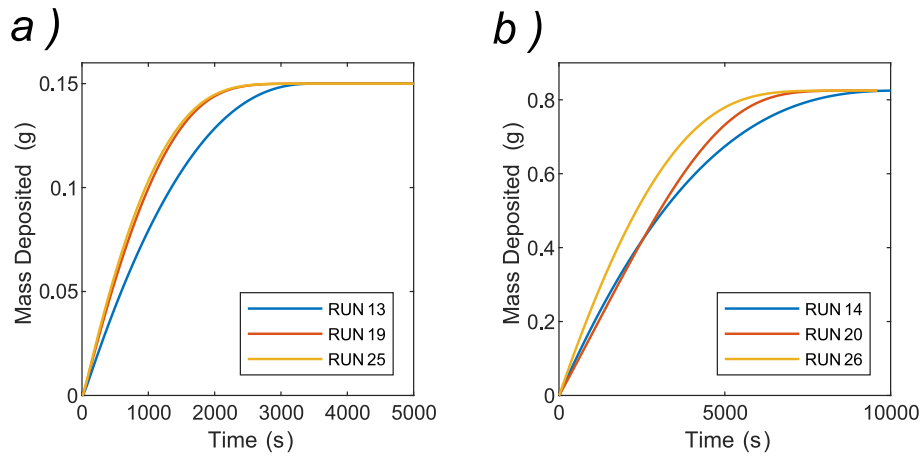


Fig. 10. Mass-time deposition curves. a) Deposition curves for runs 13,19,25. b) Deposition curves for runs 14,20,26.

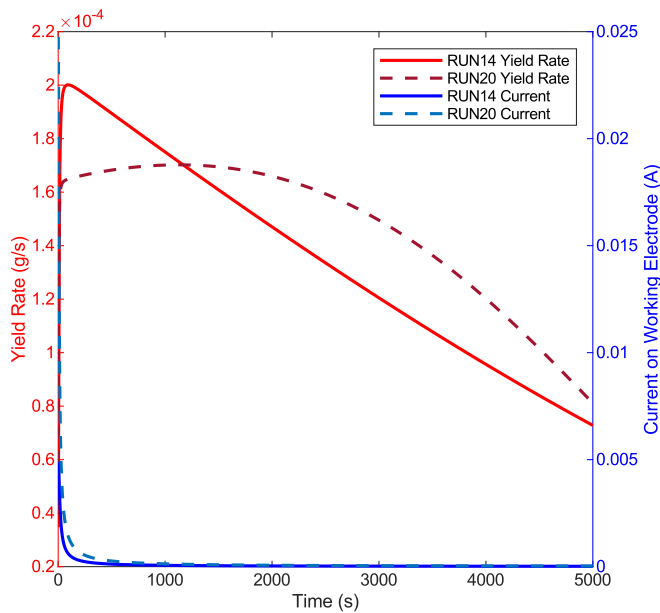


Fig. 11. Yield Rate and Current on working electrode against time for runs 14 and 20.

Where σ is the conductivity and V is the electric potential.

Neumann boundary conditions are applied to the external edges of the semi-circular domain, having form of:

$$\frac{\partial V}{\partial \eta} = 0 \quad (5)$$

where η is the outward-pointing unit vector normal to the boundary of the domain.

The density of the LiFePO_4 (ρ_{LiFePO_4}) and carbon black (ρ_{CB}) is assumed to be 3.6 g/cm^3 and 2.2 g/cm^3 [24] respectively. The electrical conductivity of the LiFePO_4 (σ_{LiFePO_4}) is taken from literature as $2.2 \times 10^{-9} \text{ (S/cm)}$ [25], as well as the one for the carbon black (σ_{CB}) as 10 (S/cm) [26].

The domain defined by the edges of the beaker, the substrate and the cylindrical electrode (Fig. 5) is meshed using 2D quadratic triangular elements with an average size of 0.15 mm.

The mesh is generated placing a number of nodes for edge 1 and edge 3 (Fig. 4) ranging from 66 to 200, depending on the dimensions of the substrate. The simulations are performed applying a constant voltage

between the cylindrical electrode and the substrate. The values of electric field and current density are used to estimate the amount of material deposited using Eq. (3). Assuming that the deposited material and the suspension are two resistances in series and neglecting the interfaces, the Electromagnetics PDE Toolbox uses an equivalent resistivity estimated at every timestep using the resistivity of the solution from the power law in Fig. 2 and the resistance of the material deposited on the substrate with the actual thickness value. The concentration of the solution is updated at every timestep to account for the decrease in concentration due to the material deposited and the corresponding increase in thickness of the material on the substrate. The equivalent resistivity is assigned to every point of the domain (Fig. 5) together with the electrophoretic mobility derived from the measurements and reported in Table 1. The flow chart with the steps is shown in Fig. 6.

The approach adopted in this work is to model the electric field at macroscopic level neglecting the effects of the interfaces between the layer of deposited material and the substrate. For this reason, even if the substrate is discontinuous, like carbon fibres, the model is applicable to describe the macroscopic behaviour and study the deposition process. The difference will be in the distribution of the electric field in the surrounding of the fibres and it will resolve in few carbon fibre diameters.

3. Scenarios simulated with the numerical model implemented in MATLAB

Minitab Statistical Software (Minitab, LLC) was used to develop an L27 orthogonal array with five parameters at three levels to conduct statistical analysis on the results obtained from the simulations. The parameters considered in the DOE are: voltage (V_{in}) in Volts, the relative weight ratio between LiFePO_4 and Carbon Black (%wt), the perimeter of the electrode (P) in cm, the length of the working electrode L_d in cm and the concentration of particles in suspension (C) expressed in g/cm^3 . The range of values selected to set the levels of the DOE is shown in Table 2.

Table 3 shows the setup of the orthogonal array, and the scenarios used in the numerical simulations for each of the 27 runs. The responses obtained from the simulations performed as part of the Taguchi DoE are:

- Yield, defined as the amount of mass deposited at a given time (g),
- Thickness, defined as the thickness of the material deposited on the substrate at a given time (cm),
- Yield Rate, defined as the mass deposited per unit time (g/s)
- Total time, defined as the time needed to fully deposit the material in the solution.

The numerical simulations provide every condition of the system at each time step (set at 1 s) from the start to the termination time, defined

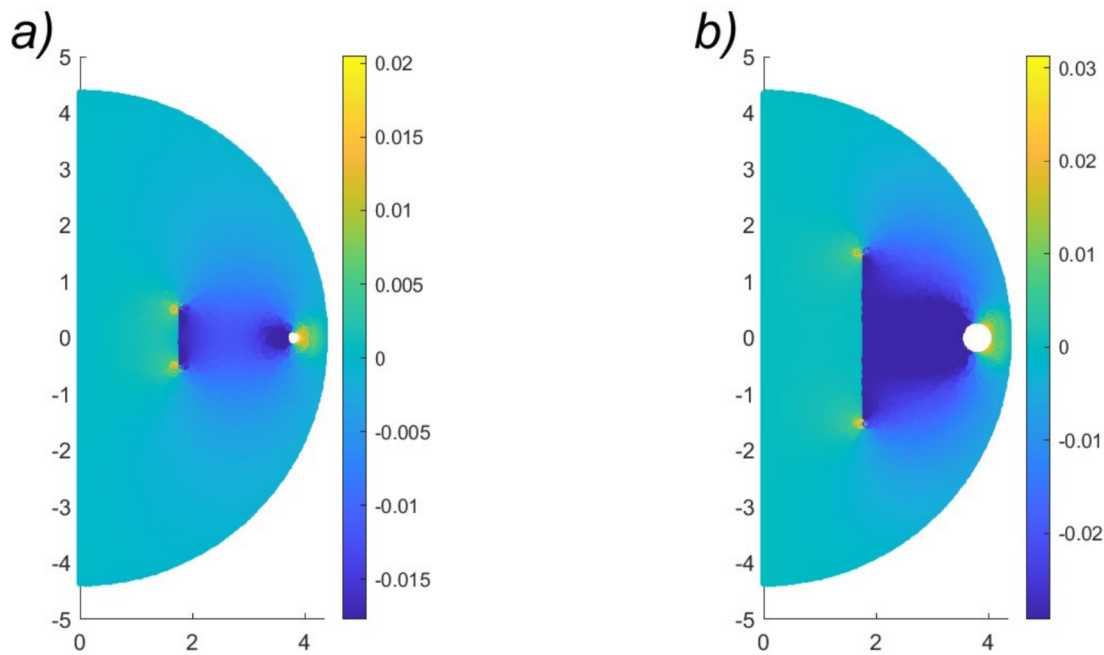


Fig. 12. Current density distribution in half-beaker. a) Distribution for run 3. b) Distribution for run 12.

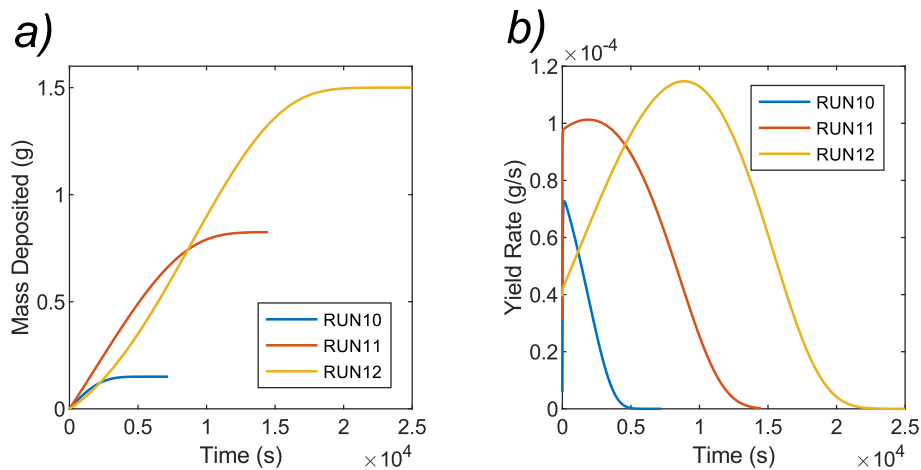


Fig. 13. Mass-time deposition curve and related yield-rate curves. a) Mass-time curves for runs 10,11,12. b) Yield rate against time for runs 10,11,12.

as the time needed to deposit 99% of the mass in solution. The responses are then analysed only at specific instant of time, namely 5 s, 1 min, 6 min, 20 min, 40 min, and 1 h. The analysis employs Taguchi methodology alongside ANOVA and regression techniques.

Taguchi S/N ratio is selected for larger-the-better conditions, which follows the equation:

$$\frac{S}{N} = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \quad (6)$$

Where Y represents the responses corresponding to the specific combination of factor levels, while n denotes the total number of responses within the said combination of factor levels.

3.1. Taguchi response analysis

Taguchi S/N responses is analysed for Yield, Thickness, and Yield Rate across six distinct time intervals, and for time of complete deposition. The main effects plots for Yield, Thickness and Yield Rate are

shown in Fig.S1.

C and V_{in} are the influential parameters in relation to Yield in the first 5 s. Between 60 and 360 s the influence of L_d and %wt become important. During the time frames of 1200 and 2400 s, while C and V_{in} remain important, the influence of L_d and %wt decreases. At 3600 s, C emerges as the most influential parameter for Yield, while P appears to be of negligible influence throughout.

Thickness shows similar trends compared to Yield, however between 60 and 360 s the influence of %wt diverges. Between 1200 and 2400 s, the trends for Thickness look similar to those of Yield. Between these time steps %wt at its highest level (85) maximises Yield, the same level does not result in a maximisation of Thickness, which is instead achieved through the intermediate level of %wt (70). This disparity may be explained by assumptions inherent in the MATLAB model, wherein deposit thickness is computed by dividing the mass deposited by density and the ratio of surface to depositing electrode length. Density is calculated from the rule of mixtures considering the relative weight ratio of the particles. Consequently, variations in density, with the deposited mass constant, result in distinct thickness outcomes. Thickness between

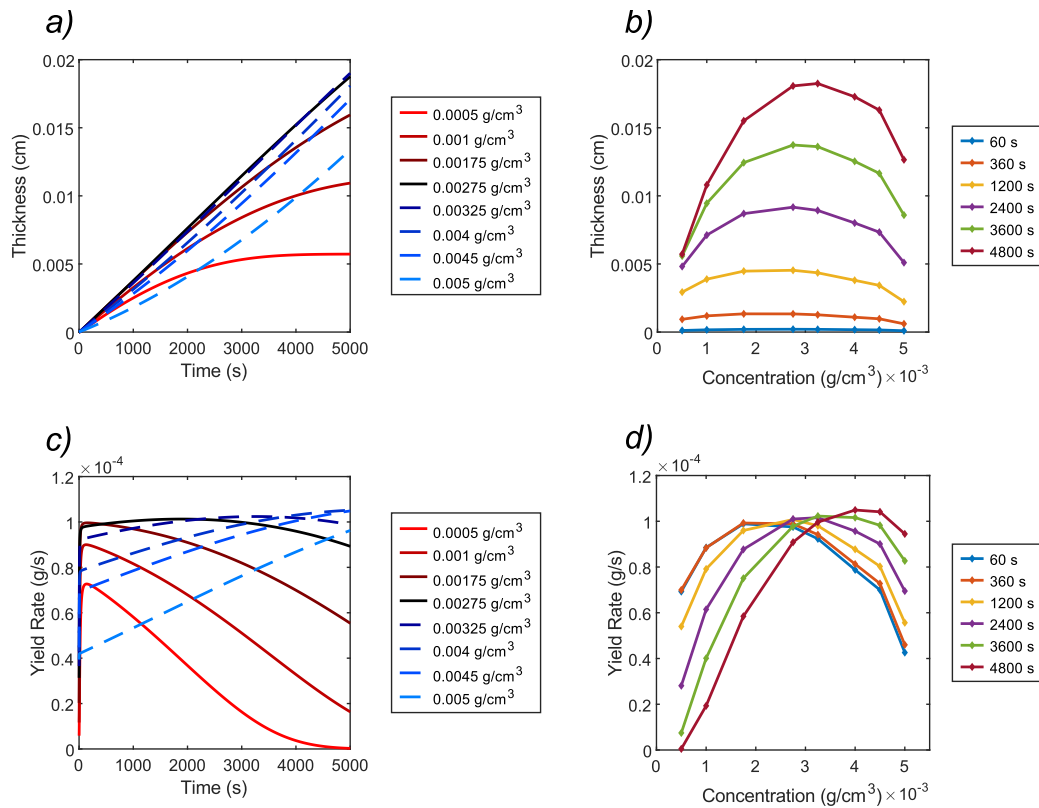


Fig. 14. Extended concentration study including runs 10,11,12. a) Thickness against time curves. b) Thickness against Concentration curves at different time steps. c) Yield Rate against time curves. d) Yield Rate against Concentration at different time steps.

2400 and 3600 s agrees with earlier trends, emphasising the significance of C , V_{in} , and L_d , while reinforcing the prementioned interrelationship between %wt and the response variables. Yield Rate closely mirrors Yield trends until 1200 s. However, C reaches peak S/N values in the latter times analysed, eclipsing the influence of other parameters. Contrasting trends between P in Yield and Yield Rate are observed, indicating a reciprocal relationship, wherein a smaller counter electrode perimeter minimally affects Yield but maximises Yield Rate. Moreover, inverted trends in V_{in} suggest that optimal Yield Rate at 3600 s is achieved through voltage reduction. This aligns with findings by Askari et al. [27], who showed that lower voltage correlates with diminished current drop, particularly during extended deposition durations. Consequently, relatively higher currents translate to higher Yield Rates, as per implications drawn from the Ferrari and Moreno model [12,13].

The Taguchi S/N ratio response for time of complete deposition is shown in Fig. 7. Here, larger the better condition for S/N was selected. The S/N ratio effect plot shows that the significant parameters are C , V_{in} , and L_d . Maximising of time of deposition is obtained through application of minimum level of V_{in} , maximum C and maximum L_d .

3.2. Regression and analysis of Variance

Assuming a normal distribution of data, the significance level, denoted as α , is conventionally set at 5%. From the ANOVA tables and regression analysis (Table S5), Fig. 8a,b,c illustrate the cumulative contributions of parameters to each response (Yield, Thickness, and Yield Rate, respectively) over the time frames examined in this study. Results are normalised with respect to the R^2 of the regression analysis and displayed in a stacked format.

ANOVA reveals a consistent trend across the three responses, namely Yield, Thickness, and Yield Rate. Initially, during the onset of EPD, the primary contributor is C , followed by V_{in} between 60 s and 360 s. During the later stages, particularly visible in Fig. 8c after 2400 s, Yield Rate is

predominantly influenced by C , with V_{in} playing a minor role, while other parameters exhibit negligible effects. For Yield and Thickness (Fig. 8a and b), the parameter L_d is statistically significant for the timesteps after 60 s, while for Yield Rate (Fig. 8c), the same parameter is significant only between 60 and 1200 s. %wt shows significance for Yield in Fig. 8a between 5 and 2400 s, for Yield Rate in Fig. 8c between 5 s and 1200 s, while it is never significant for Thickness (Fig. 8b) in these analyses.

The significance of V_{in} diminishes over time, peaking at approximately 40% during the 360 s Thickness interval (Fig. 8b), declining to a minimum of almost 5% for the 3600 s Yield Rate (Fig. 8c). On average, there is a decrease of nearly 10% in significance for both Yield (Fig. 7a) and Thickness (Fig. 8b) over time, whereas this reduction amounts to circa 20% for Yield Rate (Fig. 8c). %wt shows peaks of over 10% contribution for both Yield and Yield Rate, while its influence on Thickness remains below approximately 5%. L_d demonstrates an initial increase in contribution during the early stages of EPD, followed by a gradual decline over time, although it remains statistically significant for most analyses after the first 60 s, especially for Yield (Fig. 8a) and Yield Rate (Fig. 8c). In contrast, C consistently retains statistical significance, exhibiting an inverse trend compared to other parameters, with its importance increasing over time. C shows a peak of approximately 75% of contribution in the 3600 s Yield Rate (Fig. 8c), where the interplay between V_{in} and C is apparent. Both factors emerge as highly influential, with their normalised contributions at 5 s accounting for approximately 90% in all responses. As the deposited coating accumulates, resistance builds up, leading to a decrease in the significance of V_{in} and C . Simultaneously, other parameters such as %wt and L_d gain prominence. In the later timesteps, the impact of V_{in} decreases due to the increasing resistance of the coating, resulting in a decline in current. Consequently, C assumes greater overall significance during this phase.

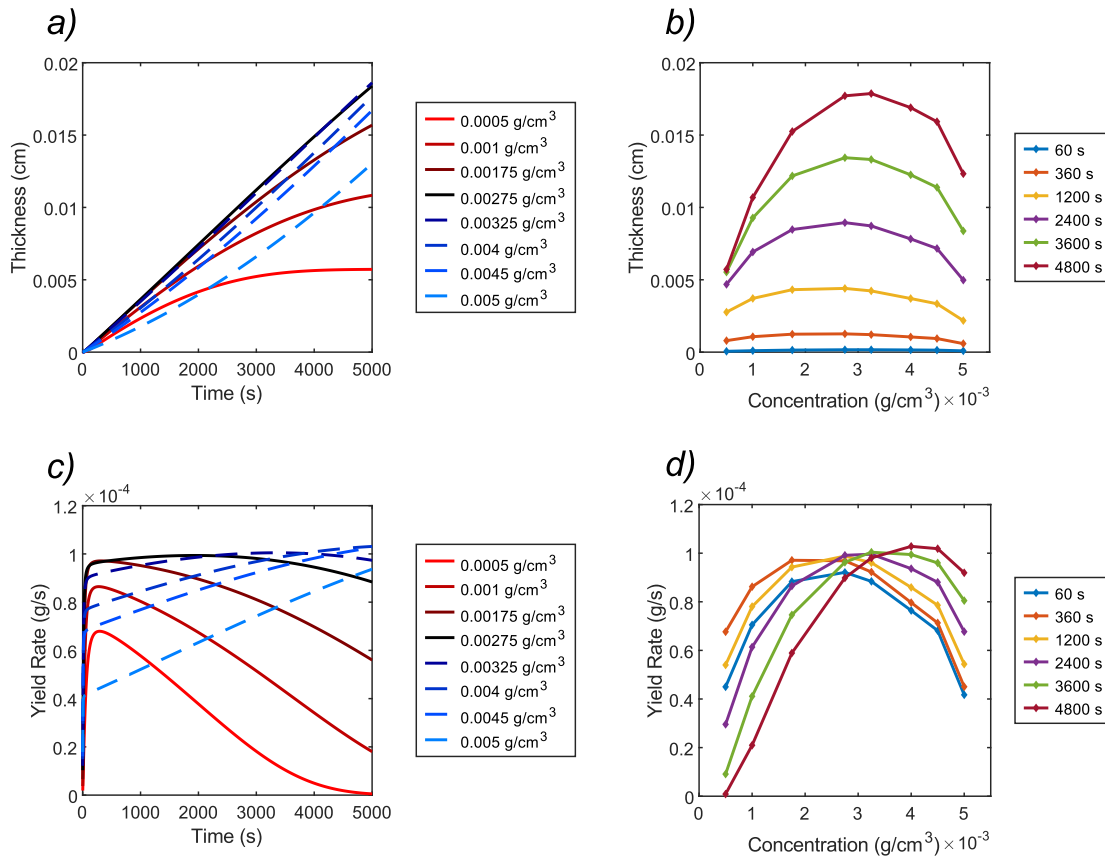


Fig. 15. Extended concentration study including runs 1,2,3. a) Thickness against time curves. b) Thickness against concentration curves at different time steps. c) Yield Rate against time curves. d) Yield Rate against Concentration at different time steps.

3.3. Mass-time deposition curves analyses

This section of the study investigates mass-time deposition curves derived from simulation runs. Several curves exhibit the characteristic S-shape as discussed by Ferrari and Moreno [13], particularly evident in higher concentrations such as in runs 3, 12, and 21, depicted in Fig. 9.

However, S-shaped curves are observed only when the $\frac{\rho_{\text{max}}}{\rho_0} > 200$, while it is in the order of tens for the others. The remaining curves predominantly align with the typical saturation curve for constant voltage and variable concentration outlined by Sarkar & Nicholson [6].

The design of the Taguchi orthogonal array dictates voltage variations across the simulation runs: the first nine employ 30 V, the next nine 70 V, and the final nine 120 V. In particular, visible in Fig. 10a, the fastest deposition times are shown by runs 25 and 19, both at 120 V. Despite differing in electrode geometry and relative weight ratios of LiFePO₄/CB, these mass-time curves largely overlap. Run 13 achieves the third fastest deposition time at 70 V, deviating from the prementioned curves in terms of relative weight ratio and electrode geometry.

In Fig. 10b runs 26, 20 and 14 are the first three to complete deposition with a concentration of 0.00275 g/cm³. Run 14 demonstrates a faster initial deposition rate compared to run 20, despite the former having a lower voltage of 70 V compared to 120 V. This difference is due to the higher yield rate observed in run 14 compared to 20, which is also linked to the sharper decrease in current observed in run 20 compared to 14. The trends for current and yield rate for both runs 14 and 20 are illustrated in Fig. 11. Run 20 begins with an initial current that is about four times higher than that of run 14, resulting in a greater amount of deposit formation, and subsequently increased resistance. This leads to a relatively more pronounced decrease in current compared to run 14.

In Fig. 9, run 3 and 12 overlap, despite run 3 being at 30 V and run 12 using 70 V. The consistent relative weight ratio in runs 3 and 12 (70/30),

indicate the possible influence of combined geometric factors on the curves. As the depositing electrode changes from approximately 1 cm to 3 cm and the counter electrode's perimeter shifts from 1 cm to 2 cm, these geometrical changes likely contribute to the observed similarities in the mass-time curves. Fig. 12a and b present the contour plots of current density for both runs 3 and 12, respectively. Despite the difference in voltage levels, the values of current density estimated in both cases are very similar. This also suggests that there is a combined influence of geometrical parameters on the current density.

Mass-time curves for runs 10, 11, and 12 are shown in Fig. 13a, while the corresponding yield rate-time curves are presented in Fig. 13b. As shown in Table 3, these runs differ solely in concentration values.

Run 12 exhibits an S-shaped trend in the mass-time curves, while runs 10 and 11 follow a saturation curve configuration. Moreover, the trajectory of the yield rate highlights distinct behaviours: for instance, the rate sharply ascends to its peak in run 10, maintains a similar trajectory in run 11 with a slight increase after the peak, whereas in run 12, the peak of the yield rate occurs approximately at 10k seconds.

3.4. Concentration effects

The observations discussed earlier prompted a deeper investigation into the influence of concentration on deposition curve trends. To explore this, consistent experimental conditions for three sets of runs are maintained, while varying particle concentration across a range of levels. Starting with the initial concentration values of 0.0005 g/cm³, 0.00275 g/cm³, and 0.005 g/cm³, an additional five intervals were introduced, resulting in a total of eight concentrations: 0.0005 g/cm³, 0.001 g/cm³, 0.00175 g/cm³, 0.00275 g/cm³, 0.00325 g/cm³, 0.004 g/cm³, 0.0045 g/cm³, and 0.005 g/cm³.

Results for thickness against time and thickness against concentration

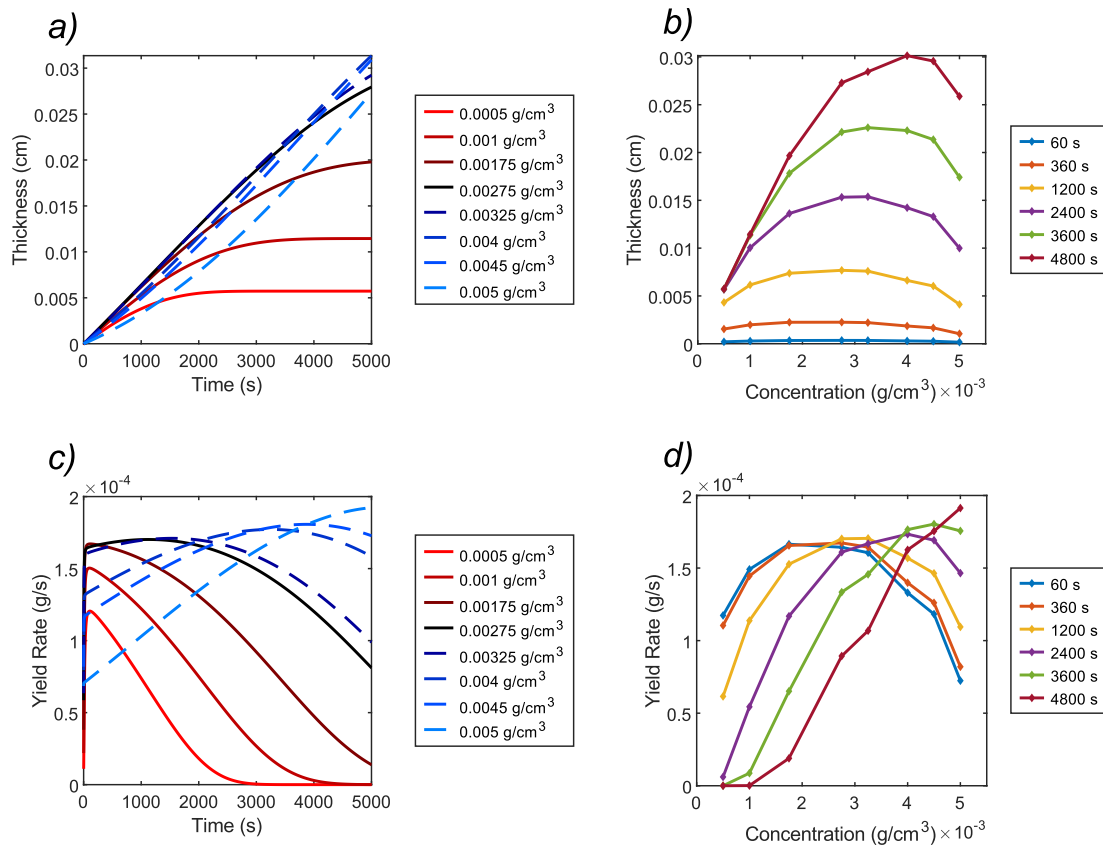


Fig. 16. Extended concentration study including runs 19,20,21. a) Thickness against time curves. b) Thickness against concentration curves at different time steps. c) Yield Rate against time curves. d) Yield Rate against Concentration at different time steps.

at a given time are shown in Fig. 14a and b, respectively. Despite its counterintuitive nature, a distinct trend emerges indicating a significant influence of concentration on the shape of the deposition curve over time (i.e., influence on yield rate). Simply increasing concentration does not necessarily lead to a proportional increase in material deposition or coating thickness. Instead, there appears to be an optimal concentration level that maximises or minimises (depending on application requirements) yield, coating thickness and yield rate in EPD. Fig. 14a shows how lower concentrations follow a typical saturation curve, where concentration increments elevate the saturation line until reaching a threshold value, here observed at 0.00275 g/cm³. Beyond this approximate threshold, further concentration increases result in a shift to an S-shaped curve, with only the initial portion shown in Fig. 14. These curves above the threshold exhibit a concave upward shape, clearly contrasting with the curves below it.

Fig. 14c displays the yield rate plotted against time. Curves representing concentrations exceeding 0.00275 g/cm³ show a consistent increase in yield rate. Conversely, those corresponding to concentrations at or below 0.00275 g/cm³ exhibit a pronounced peak during initial deposition steps, followed by a gradual decline afterwards.

Fig. 14d illustrates the relationship between yield rate and concentration across various time frames. The peak thickness is confirmed to be achieved at a concentration between 0.00275 g/cm³ and 0.00325 g/cm³, a finding corroborated by the sustained, quasi-constant yield rate observed at these specific concentration levels.

Simulations are repeated with extended concentration range for runs 1, 2, and 3, for 30 V conditions, and runs 19, 20, and 21, for 120 V, to allow a deeper understanding of optimal concentration level at different applied voltages. The results are shown in Fig. 15 for runs 1, 2, and 3, and Fig. 16 for runs 19, 20, and 21. Results for 30 V (Fig. 15) show strong similarities with results for 70 V (Fig. 14), with a semi-constant yield rate at a concentration level of 0.00275 g/cm³ (Fig. 15c), resulting in a

quasi-linear growth of thickness as displayed in Fig. 15a. Fig. 15b shows that the maximum thickness after 1200 s is obtained via concentrations ranging from 0.00275 g/cm³ and 0.00325 g/cm³, while the impact of concentration variations is less visible from deposition times including and below 360 s. Fig. 15d, shows a concentration region between 0.00275 g/cm³ and 0.00325 g/cm³, where yield rate is quasi-constant. The decrease in yield rate in concentrations exceeding this range is particularly visible in the lowest concentration value of 0.0005 g/cm³.

Upon application of 120 V, the optimal concentration for maximum thickness is obtained with concentration levels between 0.004 g/cm³ and 0.0045 g/cm³, as shown in Fig. 16a. Fig. 16b shows that after a deposition time of 2400s, the optimal concentration switched from values between 0.00275 g/cm³ and 0.00325 g/cm³, to 0.004 g/cm³ and 0.0045 g/cm³, confirmed by the trends of thickness-time curves. Fig. 16c shows that a quasi-linear yield rate over time is not obtained within the studied concentration range. In Fig. 16d the yield rate for all concentration at different time steps shows that compared to previous analyses, yield rate fluctuations over time are ampler overall, where the least variations are observed at a concentration level of 0.0045 g/cm³.

4. Conclusion

Using a numerical model in MATLAB, a combined FEM and analytical approach was developed to investigate LiFePO₄ deposition using electrophoretic deposition (EPD). Concentration is shown to be a critical factor in the deposition process, influencing the mass deposited, coating thickness, and yield rate. For different voltages, an optimal concentration level was identified to maximise thickness and yield rate, demonstrating that voltage and concentration contribute non-linearly to the outcomes.

The relative weight ratio between particles significantly affects the density of the coating and the resistivity of the suspension, as

demonstrated by ANOVA over time intervals of 1 min and 40 min. However, this weight ratio showed no impact when analysed against complete deposition time, highlighting the importance of resistivity and density in altering the deposition curve and, consequently, the yield rate.

The length of the depositing electrode also emerged as an important factor, particularly after 1 min of deposition. Mass-time curves and current distribution patterns further suggest combined effects from both the length of the depositing electrode and the perimeter of the counter electrode. Although the Taguchi design framework does not account for these combined effects, it also does not rule out the impact of varying current density distributions on the morphology of the coating.

Electrophoretic deposition (EPD) enhances the design of composite structural battery through the simultaneous deposition of structural and active materials, which unifies load-bearing and energy storage functions. The control of the thickness and microstructure allows for optimised energy density without the need for binders, which increases the active material content. Moreover, this approach enables deposition on complex geometries providing scalable, lightweight and efficient designs essential for applications in automotive.

CRediT authorship contribution statement

Stefano Russo: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Marzio Grasso:** Writing – review & editing, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Jian Huang:** Writing – review & editing, Data curation. **Stevin S. Pramana:** Writing – review & editing, Data curation. **Francesco Gucci:** Writing – review & editing. **Christopher Shaw:** Writing – review & editing. **Glenn J. Leighton:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was supported by the EPSRC Doctoral Training Partnership [grant number: EP/T518104/1] at Cranfield University, with partial funding from Polestar Automotive UK. Stefano Russo would like to express gratitude to Andreana Boatta for the input provided to the graphical abstract.

Data availability

Data supporting this study are included within the article and/or supporting materials.

References

- [1] L. Besra, M. Liu, A review on fundamentals and applications of electrophoretic deposition (EPD), *Prog Mater Sci* 52 (1) (Jan. 2007) 1–61, <https://doi.org/10.1016/j.pmatsci.2006.07.001>.
- [2] D.H. Douglas H. Everett, *Basic principles of colloid science*. Royal Society of Chemistry (1988).
- [3] J. N. Israelachvili, *Intermolecular and Surface Forces (3rd Edition)*. Elsevier, 2011. [Online]. Available: <https://app.knovel.com/hotlink/toc/id:kpISFE0003/intermolecular-surface/intermolecular-surface>.
- [4] H.C. Hamaker, Formation of a deposit by electrophoresis, *Trans. Faraday Soc.* 35 (1940) 279, <https://doi.org/10.1039/tf9403500279>.
- [5] Y. Hirata, A. Nishimoto, Y. Ishihara, Forming of Alumina Powder by Electrophoretic Deposition, *J. Ceram. Soc. Jpn.* 99 (1146) (1991) 108–113, <https://doi.org/10.2109/jcersj.99.108>.
- [6] P. Sarkar, P.S. Nicholson, Electrophoretic Deposition (EPD): Mechanisms, Kinetics, and Application to Ceramics, *J. Am. Ceram. Soc.* 79 (8) (Aug. 1996) 1987–2002, <https://doi.org/10.1111/j.1151-2916.1996.tb08929.x>.
- [7] E. Yu. Pikalova, E.G. Kalinina, Electrophoretic deposition in the solid oxide fuel cell technology: Fundamentals and recent advances, *Renew. Sustain. Energy Rev.* 116 (Dec. 2019) 109440, <https://doi.org/10.1016/j.rser.2019.109440>.
- [8] Z. Zhang, Y. Huang, Z. Jiang, Electrophoretic Deposition Forming of SiC-TZP Composites in a Nonaqueous Sol Media, *J. Am. Ceram. Soc.* 77 (7) (Jul. 1994) 1946–1949, <https://doi.org/10.1111/j.1151-2916.1994.tb07075.x>.
- [9] P.M. Biesheuvel, H. Verweij, Theory of Cast Formation in Electrophoretic Deposition, *J. Am. Ceram. Soc.* 82 (6) (Jun. 1999) 1451–1455, <https://doi.org/10.1111/j.1151-2916.1999.tb01939.x>.
- [10] M. González-Cuenca, P.M. Biesheuvel, H. Verweij, Modeling constant voltage electrophoretic deposition from a stirred suspension, *AIChE J* 46 (3) (Mar. 2000) 626–631, <https://doi.org/10.1002/aic.690460321>.
- [11] G. Anné, K. Vanmeensel, J. Vleugels, O. Van der Biest, A Mathematical Description of the Kinetics of the Electrophoretic Deposition Process for Al₂O₃-Based Suspensions, *J. Am. Ceram. Soc.* 88 (8) (Aug. 2005) 2036–2039, <https://doi.org/10.1111/j.1551-2916.2005.00387.x>.
- [12] B. Ferrari, R. Moreno, EPD kinetics: A review, *J. Eur. Ceram. Soc.* 30 (5) (Mar. 2010) 1069–1078, <https://doi.org/10.1016/j.jeurceramsoc.2009.08.022>.
- [13] B. Ferrari, R. Moreno, J.A. Cuesta, A Resistivity Model for Electrophoretic Deposition, *Key Eng Mater* 314 (Jul. 2006) 175–180, <https://doi.org/10.4028/www.scientific.net/KEM.314.175>.
- [14] A. Lavrov, Discrete-element model of electrophoretic deposition in systems with small Debye length: effective charge, lubrication force, characteristic scales, and early-stage transport, *AIMS Mater Sci* 6 (6) (2019) 1213–1226, <https://doi.org/10.3934/matrics.2019.6.1213>.
- [15] M.A. Salazar de Troya, et al., Modeling flow-based electrophoretic deposition for functionally graded materials, *Mater Des* 209 (Nov. 2021) 110000, <https://doi.org/10.1016/j.matdes.2021.110000>.
- [16] S. Datta, Application of design of experiment on electrophoretic deposition of glass-ceramic coating materials from an aqueous bath, *Bull. Mater. Sci.* 23 (2) (Apr. 2000) 125–129, <https://doi.org/10.1007/BF02706553>.
- [17] R. A. Abbas, S. A. Ajeel, M. A. Ali Bash, and M. J. Kadhim, 'Optimizing Coating Thickness of Electrophoretic Deposition Overlay on Plasma Sprayed YSZ Coating Using Taguchi Method', *IOP Conf Ser Earth Environ Sci*, vol. 961, no. 1, p. 012060, Jan. 2022, doi: 10.1088/1755-1315/961/1/012060.
- [18] G. Mohanty, L. Besra, S. Bhattacharjee, B.P. Singh, Optimization of electrophoretic deposition of alumina onto steel substrates from its suspension in iso-propanol using statistical design of experiments, *Mater Res Bull* 43 (7) (Jul. 2008) 1814–1828, <https://doi.org/10.1016/j.materresbull.2007.07.014>.
- [19] M. Sivapragash, P. Kumaradhas, B. Stanly Jones Retnam, X. Felix Joseph, and U. T. S. Pillai, 'Taguchi based genetic approach for optimizing the PVD process parameter for coating ZrN on AZ91D magnesium alloy', *Mater Des*, vol. 90, pp. 713–722, Jan. 2016, doi: 10.1016/j.matdes.2015.11.027.
- [20] B. Amir, Y. Gale, A. Sadot, S. Samuha, O. Sadot, Study on the effects of manufacturing parameters on the dynamic properties of AlSi10Mg under dynamic loads using Taguchi procedure, *Mater Des* 223 (Nov. 2022) 111125, <https://doi.org/10.1016/j.matdes.2022.111125>.
- [21] J. Hagberg, et al., Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries, *Compos Sci Technol* 162 (Jul. 2018) 235–243, <https://doi.org/10.1016/j.compscitech.2018.04.041>.
- [22] C.-C. Li, Y.-H. Wang, T.-Y. Yang, Effects of Surface-coated Carbon on the Chemical Selectivity for Water-Soluble Dispersants of LiFePO₄, *J Electrochem Soc* 158 (7) (Jul. 2011) A828–A834, <https://doi.org/10.1149/1.3592158>.
- [23] J.-P. Hsu, Y.-H. Tai, L.-H. Yeh, S. Tseng, Importance of Temperature Effect on the Electrophoretic Behavior of Charge-Regulated Particles, *Langmuir* 28 (1) (Jan. 2012) 1013–1019, <https://doi.org/10.1021/la203245n>.
- [24] Z. Chen, J.R. Dahn, 'Reducing Carbon in LiFePO₄/C Composite Electrodes to Maximize Specific Energy, Volumetric Energy, and Tap Density', *J Electrochem Soc* 149 (9) (2002) A1184, <https://doi.org/10.1149/1.1498255>.
- [25] D. Wang, H. Li, S. Shi, X. Huang, L. Chen, Improving the rate performance of LiFePO₄ by Fe-site doping, *Electrochim Acta* 50 (14) (May 2005) 2955–2958, <https://doi.org/10.1016/j.electacta.2004.11.045>.
- [26] B. Marinho, M. Ghislandi, E. Tkalya, C.E. Koning, G. de With, Electrical conductivity of compacts of graphene, multi-wall carbon nanotubes, carbon black, and graphite powder, *Powder Technol* 221 (May 2012) 351–358, <https://doi.org/10.1016/j.powtec.2012.01.024>.
- [27] N. Askari, M. Yousefpour, M. Rajabi, Determination of the optimum amount of iodine in electrophoretic deposition of hydroxyapatite (HA) nanoparticles, *J. Aust. Ceram. Soc.* 56 (3) (Sep. 2020) 1053–1059, <https://doi.org/10.1007/s41779-020-00450-8>.



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Electrophoretic deposition of LiFePO₄ and carbon black: a numerical study to explore longitudinal trends using Taguchi design

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2024-11

Elsevier

<https://doi.org/10.1016/j.matdes.2024.113446>

Russo S, Grasso M, Huang J, et al., (2024) Electrophoretic deposition of LiFePO₄ and carbon black: a numerical study to explore longitudinal trends using Taguchi design. Materials & Design, Volume 247, November 2024, Article number 113446