It is possible to simultaneously evaluate all the experimental parameters and their relative importance in a DSSC?

(Article begins on next page)

What's the correlation between dye-loading, efficiency and stability in DSC? A chemometric study on dipping conditions.

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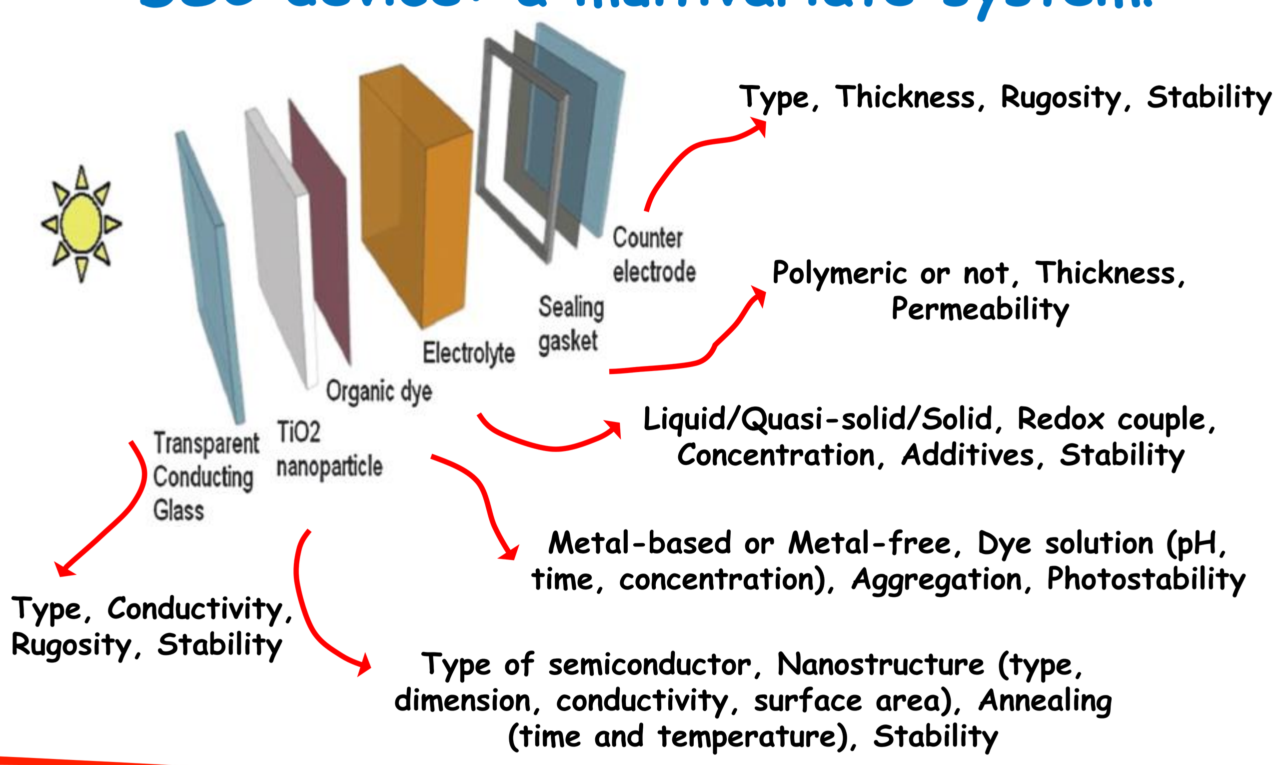
Dye-sensitized Solar Cells (DSCs), despite the continuous advances of the last years, show still a certain **difficulty in realizing devices able to guarantee at the same time**

- ✓ high photovoltaic performances
- ✓ long term stability
- ✓ reliable reproducibility

The reason is that the cells are assembled with different and heterogeneous layers, each one affected by intrinsic variability; moreover the layers influence each other. But people still perform their optimizations investigating one variable at a time.

DSC device: a multivariate system!



Design of Experiment (DoE) is a powerful technique based on multivariate mathematical models. This approach is useful for:

the interpretation of any experimental procedure in which several variables may influence the result

It allows to determine:

- ✓ significant factors
- ✓ interactions

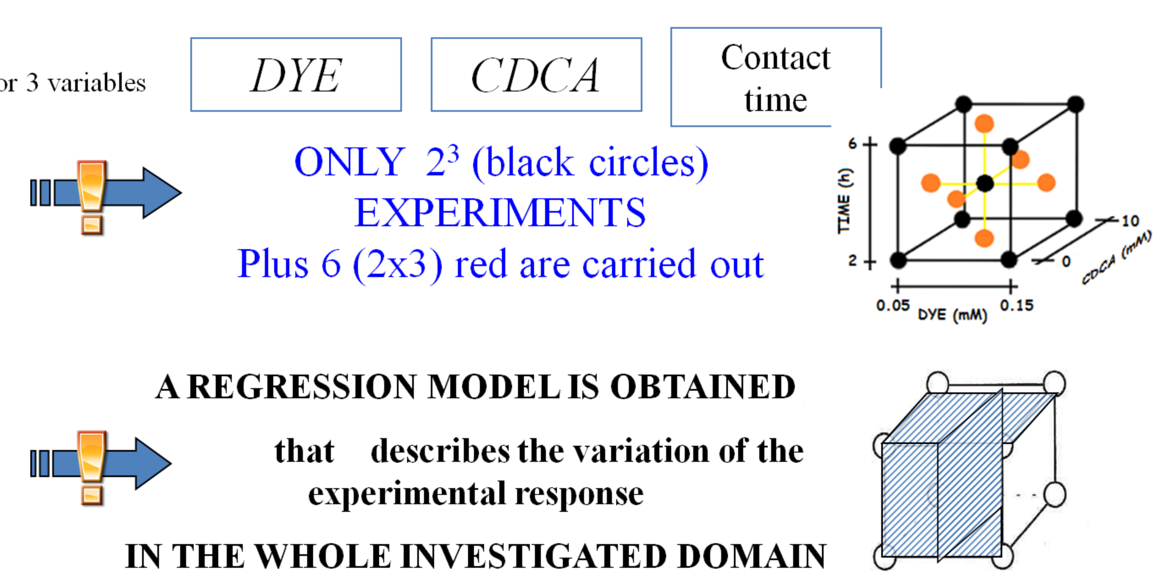
that have influence on the selected responses.

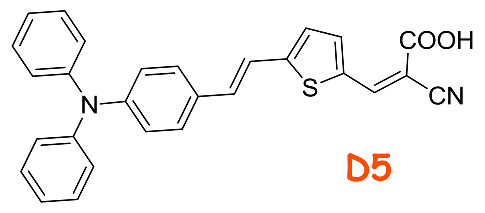
A **minimum number** of **suitable selected experiments** is needed to obtain the required information in the whole considered experimental region.

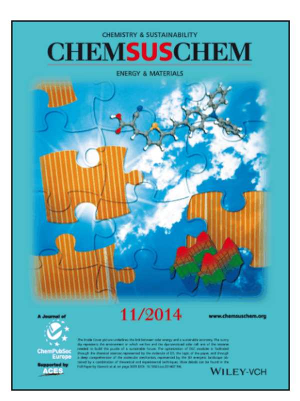
AIM OF THE WORK

The present work aims at improving the more critical PV cell parameters (dye-loading, efficiency and stability are considered the responses of the system), by studying and optimizing the DIPPING PROCESS of the photoelectrode. By a **multivariate approach**, several factors, i.e. solvent, concentration of sensitizer and co-adsorbent (CDCA), time and temperature of soaking, are taken into account **simultaneously** highlighting the importance of their INTERACTIONS. Here we present the same approach tested both on a organic (D5) and a NIR dye (VG4-C8).

D5: dye-loading optimization







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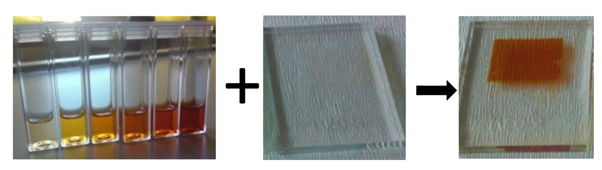
$$y = a + b_1\,D5 + b_2\,CDCA + b_3\,t + b_{12}\,D5{*}CDCA + b_{13}\,D5{*}t + b_{23}\,CDCA{*}t + b_{123}\,D5{*}CDCA{*}t$$

Main effects — Two, three factor interactions effects

Can highlight synergic and/or antagonist effects

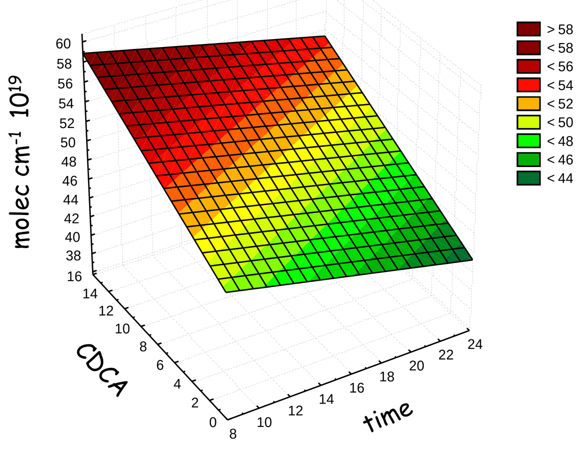


$$D5\ molec\ cm^{-3} = 28.2 + 23.1 \cdot D5 + 3.0 \cdot CDCA + 3.9 \cdot t \cdot CDCA + 2.0 \cdot D5 \cdot CDCA + 3.6 \cdot t \cdot D5 \cdot CDCA$$

Exp	t (h)	D5 (mM)	CDCA (mM)	D5 uptake (molec cm^{-3} 10^{19})
1	8	0.05	0	4,03
2	24	0.05	0	3,46
3	8	0.50	0	56,30
4	24	0.50	0	35,71
5	8	0.05	16	5,26
6	24	0.05	16	6,26
7	8	0.50	16	51,34
8	24	0.50	16	60,84
9	16	0.27	8	29,09
10	16	0.27	8	28,94
11	16	0.27	8	29,16

D5 uptake (molec cm^{-3} 10^{19})

		D5 (mM) 0.05		D5 (mM) 0.50	
CDCA (mM)	16.0	51.3	60.8	5.3	6.3
	0.0	56.3	35.7	4.0	3.5
		8.0	24.0	8.0	24.0
		t (h)		t (h)	



Take-home message: [CDCA] has **comparable** importance respect to its interaction with **time** and **dye concentration**!

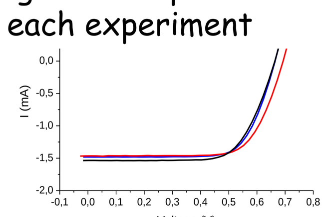
SYNERGIC EFFECT!

Toward efficiency optimization

1st STEP: to verify reproducibility and effects of fixed parameters (with statistical significance).

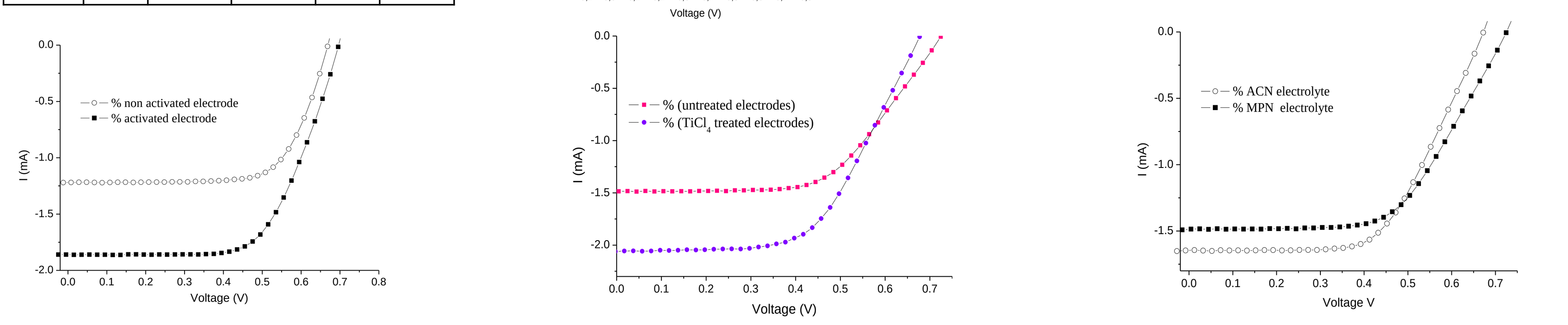
	V_{OC} (mV)	I_{SC} (mA)	FF (%)	η (%)	Dev.S.
No att	660	1,11	70,3	2,12	0,09
No att	657	1,03	68,2	1,84	0,20
Att	691	1,68	62,7	2,90	0,05
Att	688	1,82	63,2	3,09	0,09

Three genuine replicates for each experiment



ANOVA – F test

Source	Sum of squares (SS)	d.f.	MS	$F_{MSA/MSE}$
Between-groups	SSA=5.48	1	SSA/d.f.=5.48	F=143.54
Within-groups	SSE=0.95	25	SSE/d.f.=0.04	$F_{v1=1,V2=25\ \alpha=0.05}$ =4.24

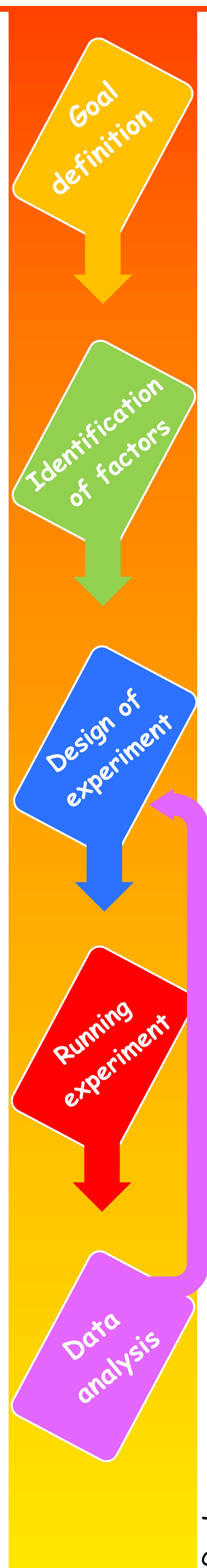


2nd STEP: to select the experimental region (see dipping conditions) and to check the CENTRAL POINT (verify the reproducibility again!).

TiO_2 thickness: 5 μm (transparent)
Electrolyte: 0.05M I_2, 0.1M LiI, 0.6M TBAI, 0.5M 4-TBP, in ACN

Reproducible result: η=3,85±0,03% (still not optimized!)

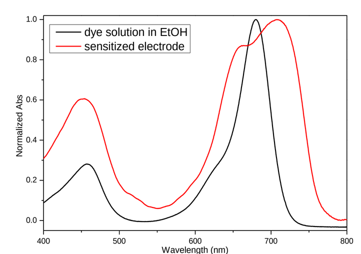
→ READY FOR MULTIVARIATE OPTIMIZATION!

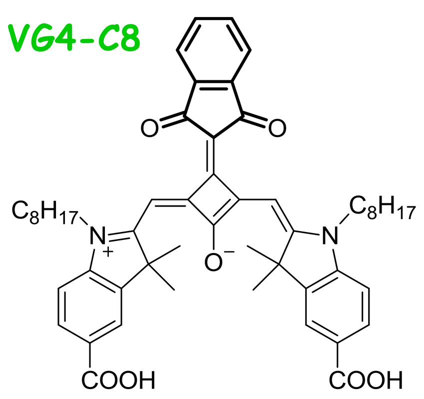


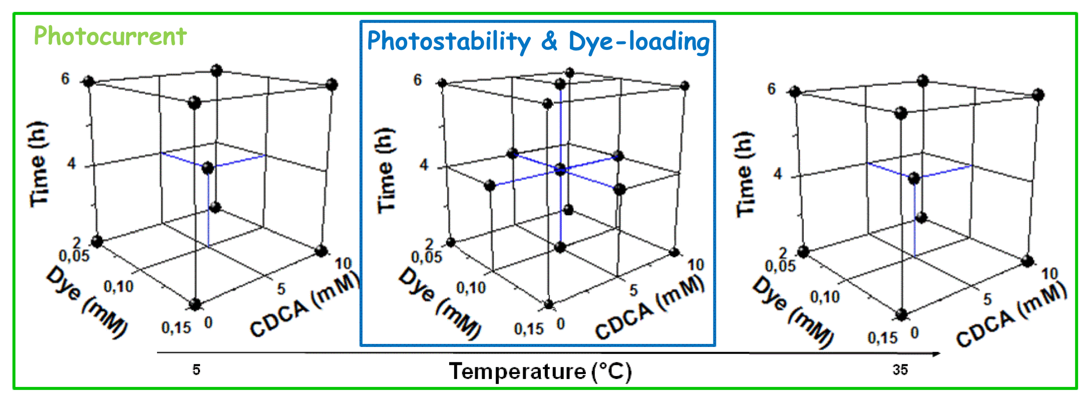
VG4-C8: dye-loading vs photostability and photocurrent

FACTORS

CDCA and **dye concentration** in dipping solution; **time** and **temperature** of dipping process.







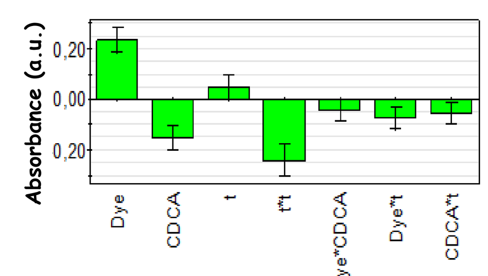
CENTRAL COMPOSITE DESIGN

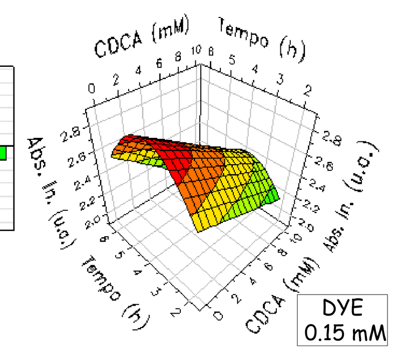
Quadratic effects are highlighted

RESPONSES

..on Dye-loading

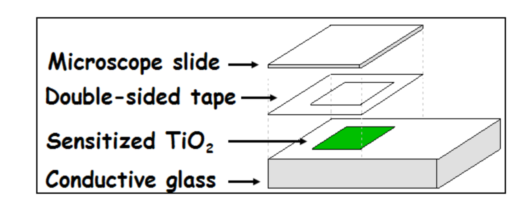
Absorbance (a.u.) of sensitized electrode.

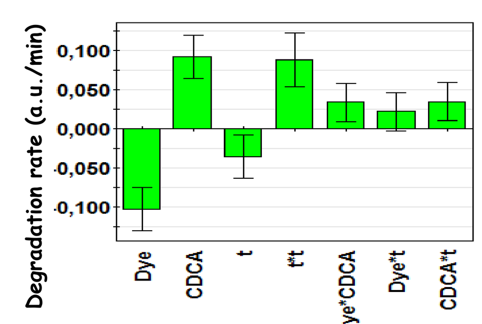


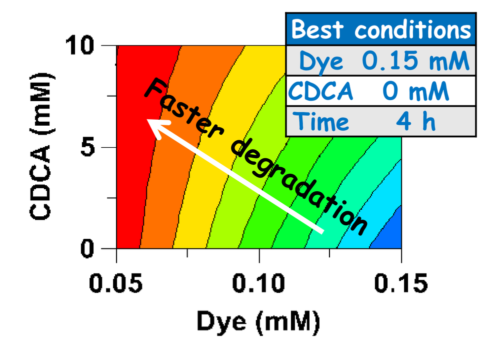


..on Photostability

Degradation rate (%), absorbance variation of the main peak in function of irradiating time on dummy cell.

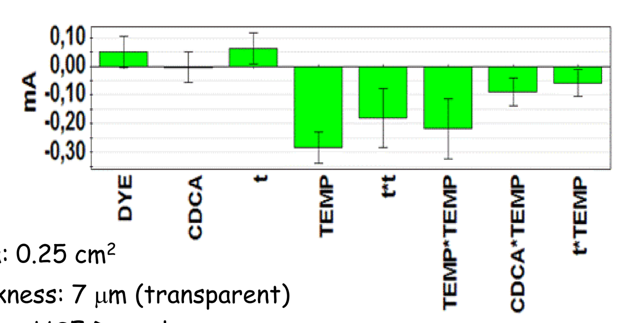




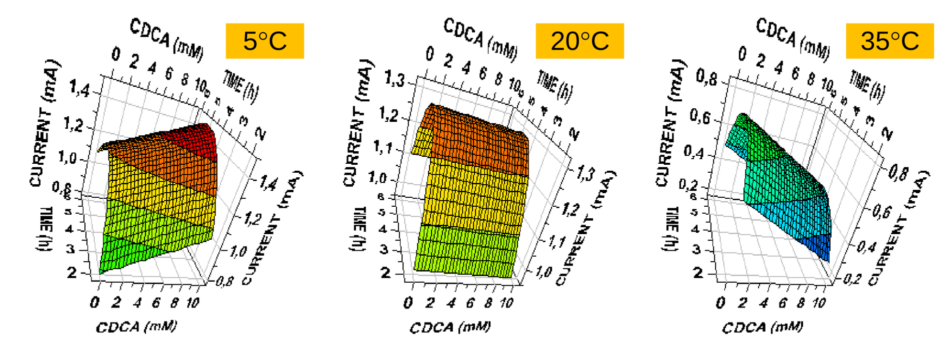


..on Photocurrent

Current (mA), measured with complete cell under standard conditions (1 Sun).



TiO_2 area: 0.25 cm^2
TiO_2 thickness: 7 μm (transparent)
Electrolyte: HSE Dyesol



Effects due to the CDCA*TEMP interaction (DYE = 0.1 mM).

CONCLUSIONS

- **Dye** concentration and dipping **time**, until 4 hours, **increase** all the responses.
- **CDCA** concentration and its **interaction** have **negative effect** on dye-loading and stability and seem not to affect the photocurrent. Really the presence of CDCA **decreases** the current at **35°C**, while at **low temperature** it has a significant **positive effect**, that enhance the maximum achievable photocurrent.
- **Temperature** is the main factor that **negative influence** the photocurrent.

This work demonstrates the power of DoE analisys to study DSC system and that the control of all conditions in dipping process is a crucial task to simultaneously improve performances, stability and reliability of DSC device.

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For more information about DoE analisys see poster P1-24