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Gravure printed cathodes for lithium-ion batteries

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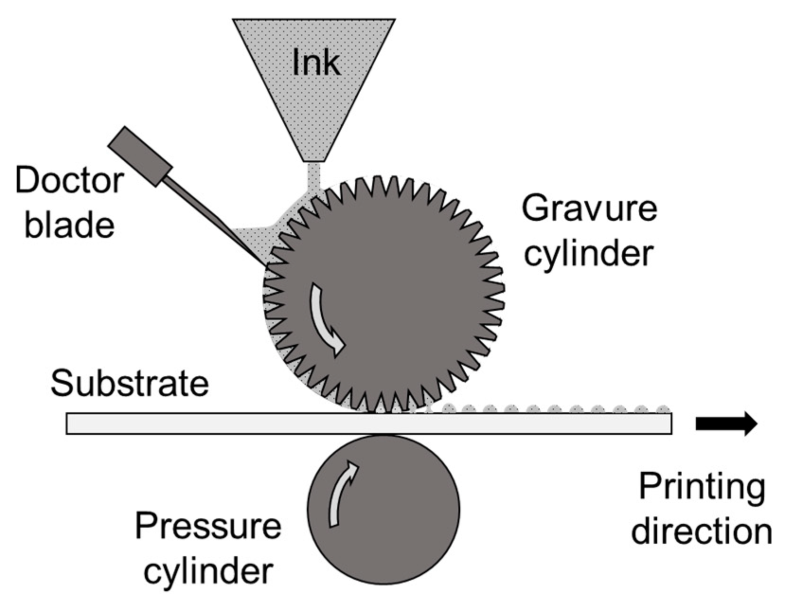
Introduction: The growing interest in printed batteries, due to their perfect customizability and integrability in everyday small devices, aimed the investigation of gravure as viable method for their production. In fact, gravure is the most appealing printing technique for the manufacturing of functional layers thanks to its unique characteristic to couple high speed and high resolution. Recently we demonstrated the possibility to use gravure printing for lithium-ion printed batteries, successfully manufacturing electrodes and answering to many challenges related to the selected printing technique. In this work a comparison of cathodes based on two different active materials (LFP and LMO) is reported to test the ink preparation and printing methodology based on the Capillary number.

Method:



The fluid-dynamic of the gravure can be described at microscopic level by a dimensionless number, named Capillary number (Ca), directly depending on the viscosity forces (ηU), which impede the ink flow, and inversely depending on the surface tension forces (γ), which are the driving forces [1]:

$$Ca = \eta U/\gamma$$

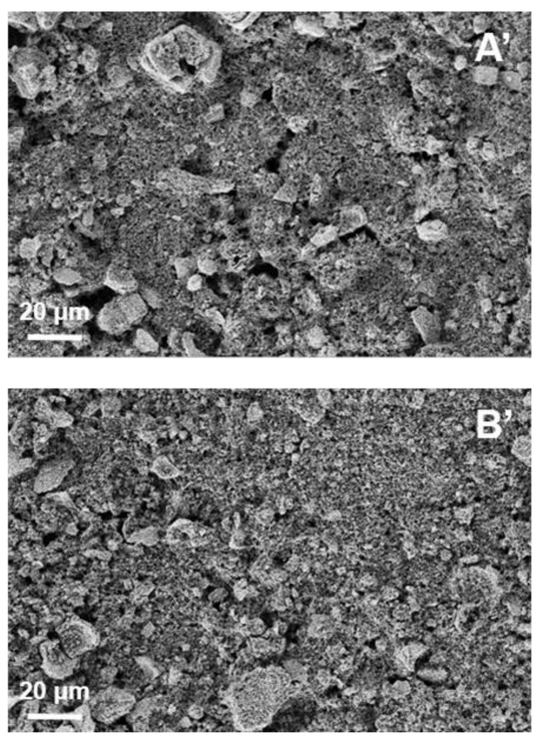
It was observed that the best printing quality is obtained when the Ca is closed to 1 [2-4]. This represents the base to develop the methodology for ruling the gravure ink formulation and the printing parameters.

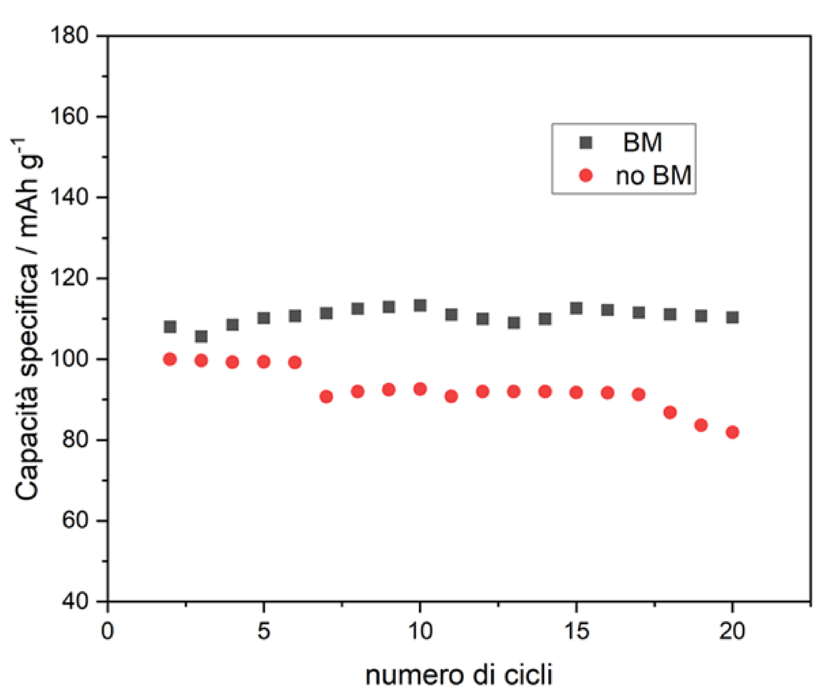
Experimentally:

ink preparation ➡ ink characterization ➡ printing test ➡ ink/layer optimization ➡ test in device

LMO based cathodes:

Dry solid content [wt%]	Ball milling	Printing speed [m/min]	Printing force [N]	Ca	Mass loading [mg/cm^2]	Thickness [µm]
18	No	12	700	0.4		
18	Yes	12	700	0.4		
18	No	36	700	1.1	0.7	19±4
18	Yes	36	700	1.2	2.0	24±2
18	No	60	700	1.9		
18	Yes	60	700	2.1		

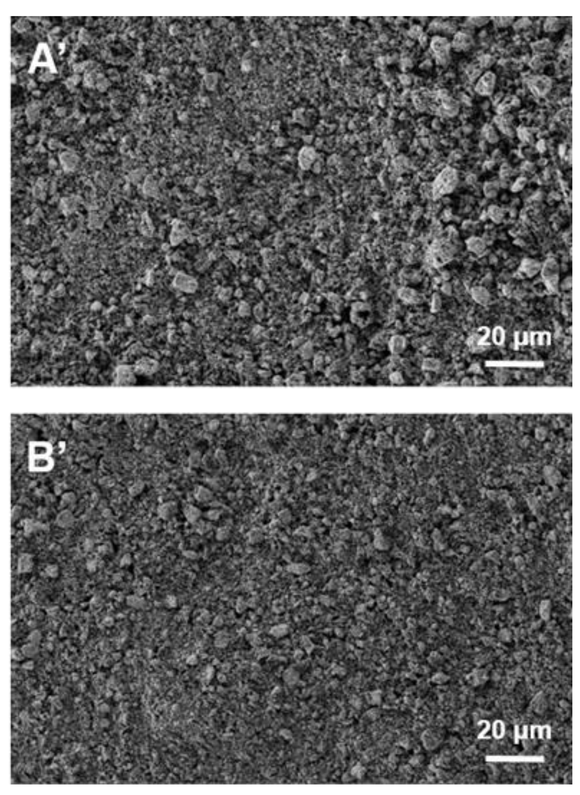


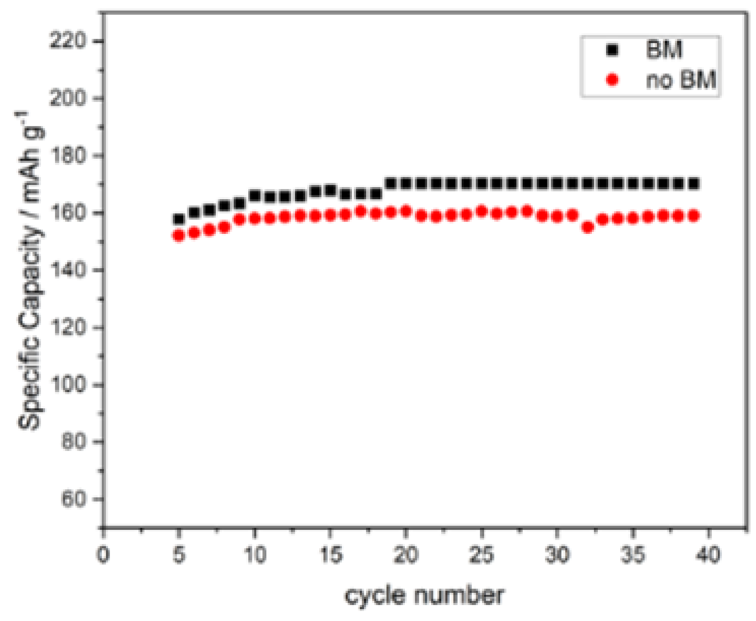


The printed layer using Ca approaching the unity showed a good printing quality and displayed a proper functionality. The ball-milling improved the cathode performance increasing the layer density. However the specific capacity was found lower than the theoretical value.

LFP based cathodes:

Dry solid content [wt%]	Ball milling	Printing speed [m/min]	Printing force [N]	Ca	Mass loading [mg/cm²]	Layer thickness [µm]	Apparent layer density [g/cm³]
15	No	12	700	0.5			
15	Yes	12	700	0.3			
15	No	36	700	1.5	1.8 ± 0.2	20 ± 1	0.90
15	Yes	36	700	0.8	1.4 ± 0.2	15 ± 1	0.93
15	No	60	700	2.4			
15	Yes	60	700	1.4			





The printed layer using Ca approaching the unity showed a good printing quality and displayed a proper functionality. The ball-milling slightly improved the capacity which was found closed to the theoretical value.

Conclusion: The multilayer approach allowed to obtain a mass loading suitable for practical applications also providing high homogeneity. A methodology for ruling the ink formulation and process parameters based on the Capillary number was proposed and validated, providing a high printing quality thus the layer functionality. Nevertheless, specific parameters, such as contribution of mass loading, component ratio, material size, component distribution, and layer density have to be considered for achieving high performance layers.

References:

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