Italian National Agency for New Technologies, Energy and Sustainable Economic Development

Stampa rotocalco per la produzione di batterie Litio-ione e Sodio-ione

M. Montanino

Outlines

- Introduction on printed batteries
- Gravure printing overview
- Our contribution: a methodology for ink formulation and process
- AdP 2022-2024 main results: Li-ion and Na-ion batteries manufacturing
- Conclusions

Printed batteries

- More and more involved in the growing area of small, wearable and portable electronic devices needing on-board power supply. For this propose, batteries have to be highly customizable to be perfectly integrated into the electronic device. Moreover, their production could be integrated in-line to the manufacturing of printed electronics devices.
- Typical capacities of 5–10 mAh cm^{-2}
- Overall dimension below $10mm^3$

Printing technologies offer the possibility to produce low-cost thin, flexible and arbitrary shapes different functional layers and devices (even in case of multifunctional layered structures), at high throughput also in large area, with high layer control, homogeneity and reproducibility, especially when compared to coating techniques.

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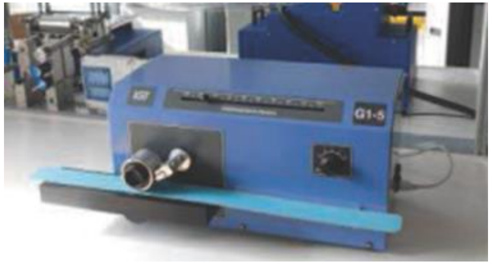
Gravure printing

- ➢ ***Why gravure?***
  - ✓ Ability to couple ***high throughput*** (up to 600 m/min) and ***high quality*** (resolution and register ≈ 0,1µm)
  - ✓ Industrially widespread (graphics, packaging, currency,…) easy to ***scale-up***
  - ✓ Highly ***sustainable*** (low waste of energy and materials, possibility to ***recover solvents***)
  - ✓ Possibility of ***arbitrary shapes (2D)***
  - ✓ Possibilty of ***tuning*** the layer structure/properties
  - ✓ ***Flexible substrates***
  - ✓ ***Large printing area*** (web width up to 2m)

Industrial scale



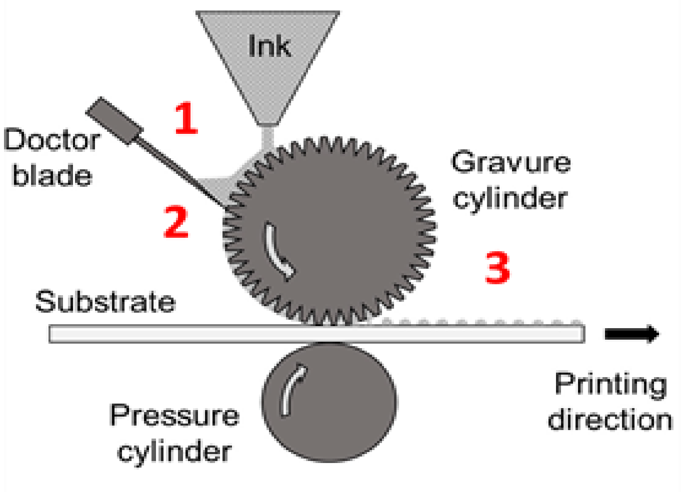
lab scale

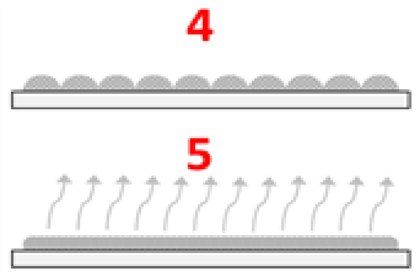
Gravure process

The process consists of the direct transfer of ink from the engravings of a printing cylinder onto a flexible substrate thanks to the pressure of a counter cylinder.

The process can be described as a series of sub-processes, each one having its ideal operating regime, concurring to determin the final quality of the printed layer.

1. *Inking*
2. *Doctoring*
3. *Transfer*
4. *Spreading*
5. *Drying*





Main involved parameters

The final printing quality depends on the interplay of many parameters

Gravure Cylinder	Process	Ink	Substrate
Cell geometry	Printing force	Viscosity	Surface energy
Cell density	Printing speed	Surface tension	Roughness
Surface energy	Web tension	Solvent eveaporation rate	porosity
diameter		Solid content	

Complex process, not easy modelling

The dimensionless analysis is used for simplifying the study of the process:

Capillary number (Ca) = printing speed x ink viscosity / ink surface tension

Our contribution

Recently, we demonstrated the possibility to succesfully gravure print both anodes and cathodes, showing high performances with capacity closed to the theoretical values, long life cyclability, stability, high reproducibility

- Montanino, M.; Sico, G.; De Girolamo Del Mauro, A.; Moreno, M. LFP-Based Gravure Printed Cathodes for Lithium-Ion Printed batteries. Membranes **2019**, 9, 71.
- Montanino, M.; Sico, G.; De Girolamo Del Mauro, A.; Asenbauer, J.; Binder, J.R.; Bresser, D.; Passerini, S. Gravure-Printed Conversion/Alloying Anodes for Lithium-Ion Batteries. Energy Technol. **2021**, 9, 2100315.
- Montanino, M.; De Girolamo Del Mauro, A.; Paoletti, C.; Sico, G. Gravure Printing of Graphite-Based Anodes for Lithium-Ion Printed Batteries. Membranes **2022**, 12, 999.
- Montanino, M.; Paoletti, C.; De Girolamo Del Mauro, A.; Sico, G. The Influence of the Gravure Printing Quality on the Layer Functionality: The Study Case of LFP Cathode for Li-Ion Batteries. Coatings **2023**, 13, 1214.
- Montanino, M.; Paoletti, C.; De Girolamo Del Mauro, A.; Sico, G. Gravure printed composites based on Lithium Manganese Oxide: A study case for Li-ion batteries manufacturing. Macromol. Symp. **2024**;
- Montanino M.; Sico G. Gravure printing for Lithium-Ion Batteries Manufacturing: A Review. Batteries **2023**,9, 535.

Our metodology: ink formulation and high printing quality

Modelling ink formulation could promote at industrial level gravure printing for batteries manufacturing

Challenges: difficulty to realize composite layer displaying proper functionality using low viscosity inks. Difficult to achieve mass loading suitable for practical use

To obtain high printing quality:

- viscosity < 100 mPas; ink surface tension < surface energy of the substrates and of the printing cylinder
- Systematic study to produce gravure printable inks for the manufacturing of electrodes for lithium-ion batteries, selecting functional components (solids) and process components (solvents), their amount and relative quantities, taking into account the specific range of each component, in way to have ink solid content < 25 wt%
- Capillary number = printing speed x ink viscosity / ink surface tension ≈ 1

Result: Obtaining an experimental database which will be used through the capillary number methodology to provide the best ink formulation recipe as output

NOTE: High capacity materials would enable the use of such technique also to different field and applications, especially considering that the deposition method thus the layer quality have a great influence on the layer performances, having the same importance of the materials.

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Risultati batterie Li-ione

- Studio e formulazione di inchiostri a base di materiali attivi anodici e catodici acquistati durante LA1.11 con diversi leganti e solventi
- Stampa di elettrodi a base di LFP (con CMC e acqua) a larga area (≈20 cm^2) e test statistici morfologici per verificare omogeneità in scale-up.
- Caratterizzazione elettrochimica deli elettrodi stampati a base di LFP di larga area (≈20cm^2)
- Studio e caratterizzazione inchiostri a base di $LiNiMnCoO_2$ commerciale (MNC 1,1,1)(con Acqua e CMC); Studio e formulazione di inchiostri a base di materiale attivo catodico $LiNiMnCoO_2$ commerciale (MNC 1,1,1) con diversi leganti e solventi
- Stampa di strati catodici a base di $LiNiMnCoO_2$ commerciale (MNC 1,1,1) (con CMC e acqua) e loro caratterizzazione morfologica ed elettrochimica

Li-ion batteries: large area test (up to 20 cm^2)

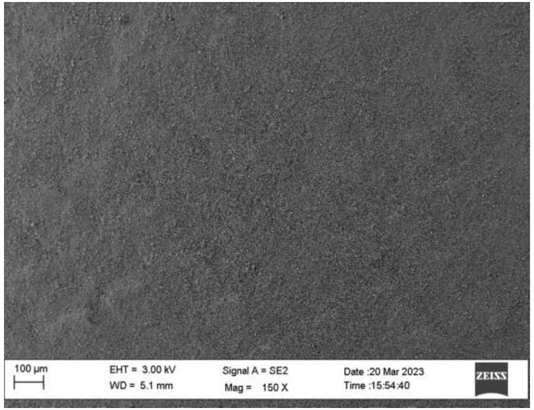
Experiments:

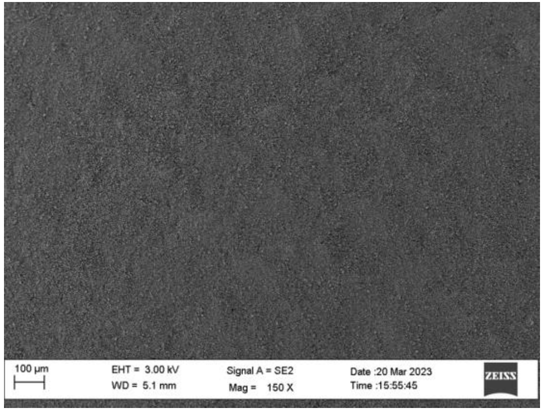
- Active material: LFP; Binder: CMC; solvent: water/isopropanol (80/20) wt/wt%);
- ink formulation based on the Ca ≈ 1.
- Ink: solid content of 15 wt%
- short ball-milling (3 min)
- Printing: on aluminum foil, overlapping up to 15 layers of same ink in same conditions
- Achievement of practical mass loading through layers overposition (1.8 mg/cm^2)
- SEM images for statistic test of homogeneity
- Test in half-cell vs Li (in progress)

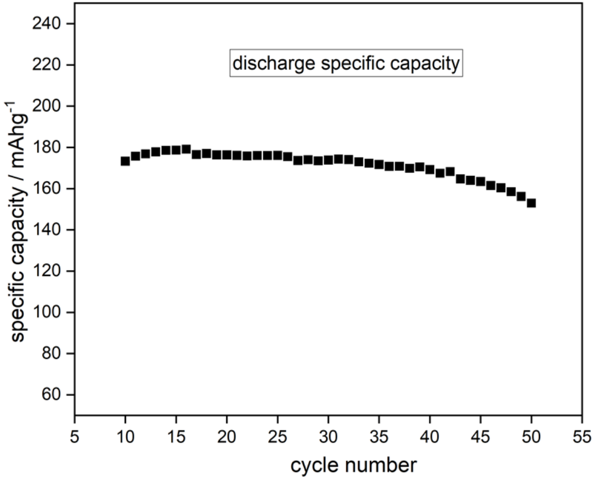
Li-ion batteries: large area test (up to 20 cm^2)

Results:

High printing quality and homogeneity







Good electrochemical performance

Future work: investigation on long life cyclability and reproducibility also @ different rate

Li-ion batteries: High performace material: NMC111

Experiments:

Dry content %	***Dry content Composition***	***Solvent***	***BM***	***Viscosity***
15	88% MA 6% super P 6% CMC	H2O-IPA 90/10	No	90
15	88% MA 6% super P 6% CMC	H2O-IPA 90/10	5’	270
15	80% MA 10% super P 10% CMC	H2O-IPA 90/10	No	309
25	88% MA 6% super P 6% PVDF-HFP	cicloesanone	No	-
15	88% MA 6% super P 6% PVDF-HFP	cicloesanone	No	
5	88% MA 6% super P 6% PVDF-HFP	cicloesanone	No	290
5	88% MA 6% super P 6% PVDF-HFP	Acetone/DMSO 70/30	No	
15	88% MA 6% Grafite 6% PVDF-HFP	cicloesanone	No	

Li-ion batteries: High performace material: NMC111

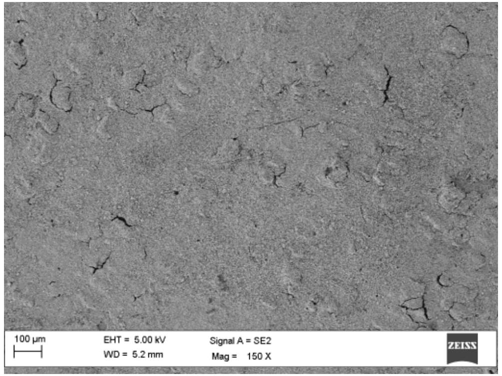
Experimental:

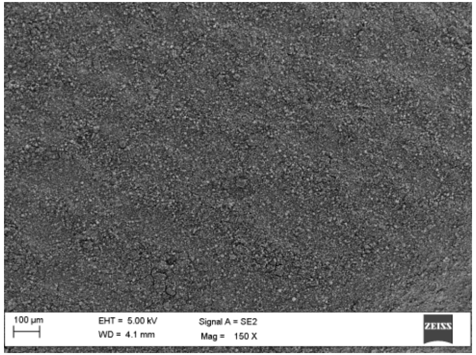
Dry content %	***Dry content Composition***	***Solvent***	***BM***	***Viscosity***
15	88% MA 6% Grafite 6% PVDF-HFP	Acetone/DMSO 70/30	No	
10	88% MA 3% super P; 3% Grafite 6% PVDF-HFP	Acetone/DMSO 70/30	No	
10	88% MA 6% KJB 6% PVDF-HFP	Acetone/DMSO 70/30	No	
18	88% MA 6% KJB 6% PVDF-HFP	Acetone/DMSO 70/30	5’	
22	88% MA 3% KJB; 3% Super P 6% PVDF-HFP	cicloesanone	30’	95.5
15	88% MA 3% KJB; 3% super P 6% PVDF-HFP	cicloesanone	30’	
22	88% MA 3% KJB; 3% super P 6% CMC	H2O/IPA 85/15	30’	180
18	88% MA 3% KJB; 3% super P 6% CMC	H2O/IPA 85/15	30’	93

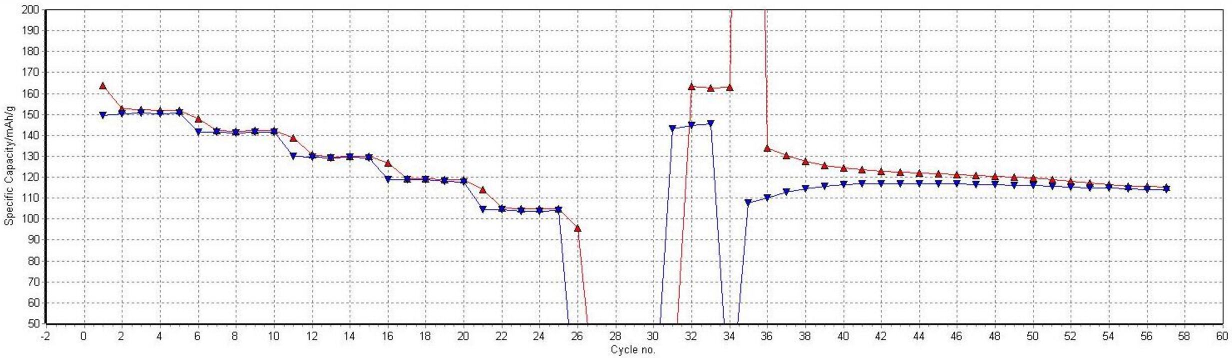
Li-ion batteries: High performace material: NMC111

Results:

High printing quality







Good electrochemical performance

Future work: investigation on long life cyclability

Na-ion batteries

- The important results obtained for the Li-ion batteries (LiBs) encouraged us to investigate the possibility to employ gravure printing for different storage systems, beyond the Lithium chemistry, such as the Sodium batteries (NaBs).
- NaBs are investigated as an alternative to LiBs for the large scale electrochemical storage due to the intrinsic characteristics of Sodium, which is economic, abundant and ecofriendly.

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Risultati batterie Na-ione

- Scelta dei materiali e loro acquisto
- Studio e formulazione di inchiostri a base di materiali attivi anodici e catodici acquistati durante LA1.14 con diversi leganti e solventi
- Studio materiale attivo per catodi: $NaLiNiMnO_2$ da sintesi enea
- Studio e caratterizzazione inchiostri a base di $NaLiNiMnO_2$ (con Acqua e CMC)
- Realizzazione catodi stampati (≈1,5 mg/cm^2)
- Caratterizzazione morfologica ed elettrochimica dei catodi stampati
- Studio e formulazione di inchiostri a base di materiale attivo catodico $NaLiNiMnO_2$ da sintesi enea con PVDF-HFP
- Studio e formulazione di inchiostri a base di materiale attivo anodico Hard Carbon commerciale (BHC-300) (con acqua e CMC)
- Stampa di strati anodici a base di Hard Carbon commerciale (BHC-300) e loro caratterizzazione morfologica ed elettrochimica

Na-ion batteries: first attempt of cathode

Intent: to obtain a high printing quality of the cathode through the Ca methodology and to verify its functionality

Active material: NaLi0,2Ni0,25Mn0,75O2 produced in our laboratory by a scale-up method

Sustainability: For the production of the gravure printed cathodes, the water soluble carboxymethyl cellulose was chosen as binder, thus allowing to use water as prevalent solvent, enhancing the sustainability of the production process and of the electrode itself

Ink:active material (80%), Sodium salt of the carboxymethyl cellulose (CMC) (10%) as binder and carbon Super P as electric conductor (10%)

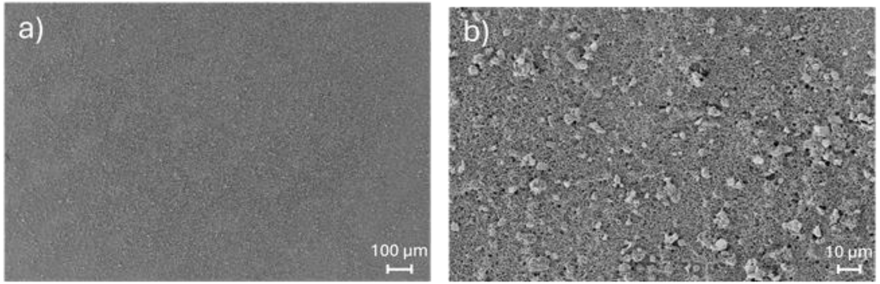
Solvent: mixture of water and 2-propanol (90/10 wt/wt%)

Best printable ink: 15 % of solid content had best viscosity was (75 mPa s). The Ca was calculated 1.1 at a printing speed of 36 m min-1 thus, such speed was used for printing layers.

Print: 10 overlapped layers on Al foil

Na-ion batteries: first attempt of cathode

- good coverage and high homogeneity of the printed layer without critical defects such as voids, scratches, undulations



- Achievement of cathodic functionality thanks to the high printing quality
- Poor electrochemical performances due to specific issues related to the active material such as sensitivity to water, oxygen moisture and CO2 even when exposed to not controlled environment
- The effect of these environmental agents on the structure and the electrochemical performance of such materials makes necessary stabilization strategies, for not decreasing their potential capacity when used in an industrial ambient manufacturing process

Na-ion batteries: gravure printed HC-based anodes

- ✓ Hard carbon BHC-300, was provided by MTI Corporation
- ✓ Inks: active material (88%), Binder Sodium salt of the carboxymethyl cellulose (CMC) (6%), electric conductor carbon Super P.
- ✓ Solvent: mixture of water and 2-propanol (90/10 wt/wt%)

solid content wt%	η @ 20°C mPa s	U $mmin^{-1}$	Ca
18%	138	36	1.97
		24	1.31
		12	0.66
15	83	36	1.18
		24	0.80
		12	0.40
14	70	36	1.00
		24	0.67
		12	0.34

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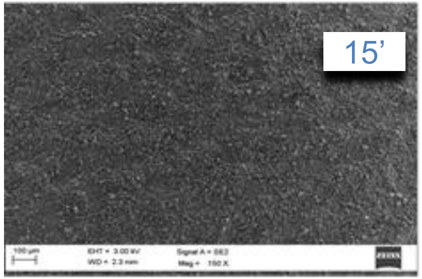
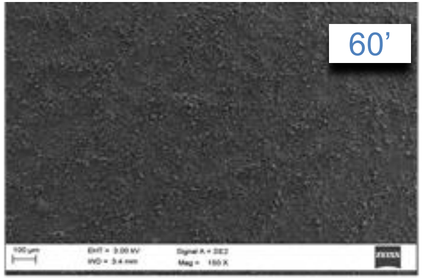
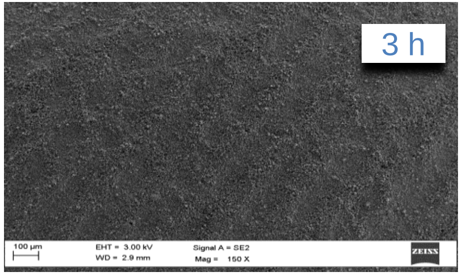
Na-ion batteries: gravure printed HC-based anodes

✓ Printed layer characteristics

Ink/BM time	Mass loading mg/cm^2	Active material mg/cm^2	Thickness cm	Porosity volume%
15’	0.80	0.70	$26\ 10^{-4}$	83 %
60’	0.94	0.83	$26\ 10^{-4}$	81 %
3h	0.92	0.81	$20\ 10^{-4}$	75 %







- 15’ ball milled ink shows an irreversible capacity in the range of 400-440 mAh/cm2 for the first 20-30 cycles, following a drop in capacity to 130 mAh/cm^2 can be observed . The reversible capacity of 130 mAh/cm^2 is stable over 100 cycles cycling at fixed C/10.
- 60’ and 3h don’t show the irreversible part of the capacity, having from the beginning a reversible capacity in the range of 120-100 mAh/cm2, stable over 100 cycle at fixed C/10 rate.

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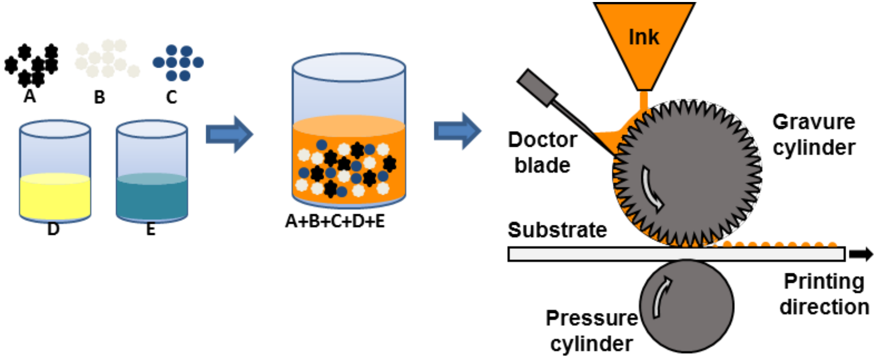
Conclusions

- ✓ Gravure printing is a ***very appealing*** technique for the low-cost arbitrary shape manufacturing of high quality functional layers, also as electrodes for batteries
- ✓ We demonstrated the possibility to use the sustainable and industrial large-area gravure printing for ***batteries manufacturing***
- ✓ ***Many challenges*** related to the printing technique have been ***addressed***
- ✓ The ink formulation and the choice of process parameters are ruled by a ***methodology based on the Ca*** able to guarantee a good printing quality thus the layer functionality
- ✓ To achieve good layer ***performances specific issues*** (related to materials, type of electrode…) have to be considered

Thanks for your kind attention

maria.montanino@enea.it

Our experimental activities



- Preliminary studies of the inks and substrates (ink and substarte wettability, substrate roughness, substrate pre-treatments)
- Formulation and characterization of inks suitable for gravure (ink rehological behaviour, solvents choice and behaviour, concentration, proper mixing and dispersing processes)
- Optimization of printing process parameteres (speed, pressure, multilayering, drying)
- Off-line post-processing steps
- Morphological and electrical characterization of the printed layer
- Tests of performance in battery