Laboratorio di Elettrochimica
dei Materiali per l'Energetica

"Water processable polymers for supercapacitors and Li-ion batteries

Francesca Soavi,
Alessandro Brilloni, Federico Poli, Daniele Marchese, Giovanni E. Spina

LEME - Laboratory of Electrochemistry of Materials for Energetics
Department of chemistry "Giacomo Ciamician"
http://www.ciam.unibo.it/leme
Alma Mater Studiorum University of Bologna

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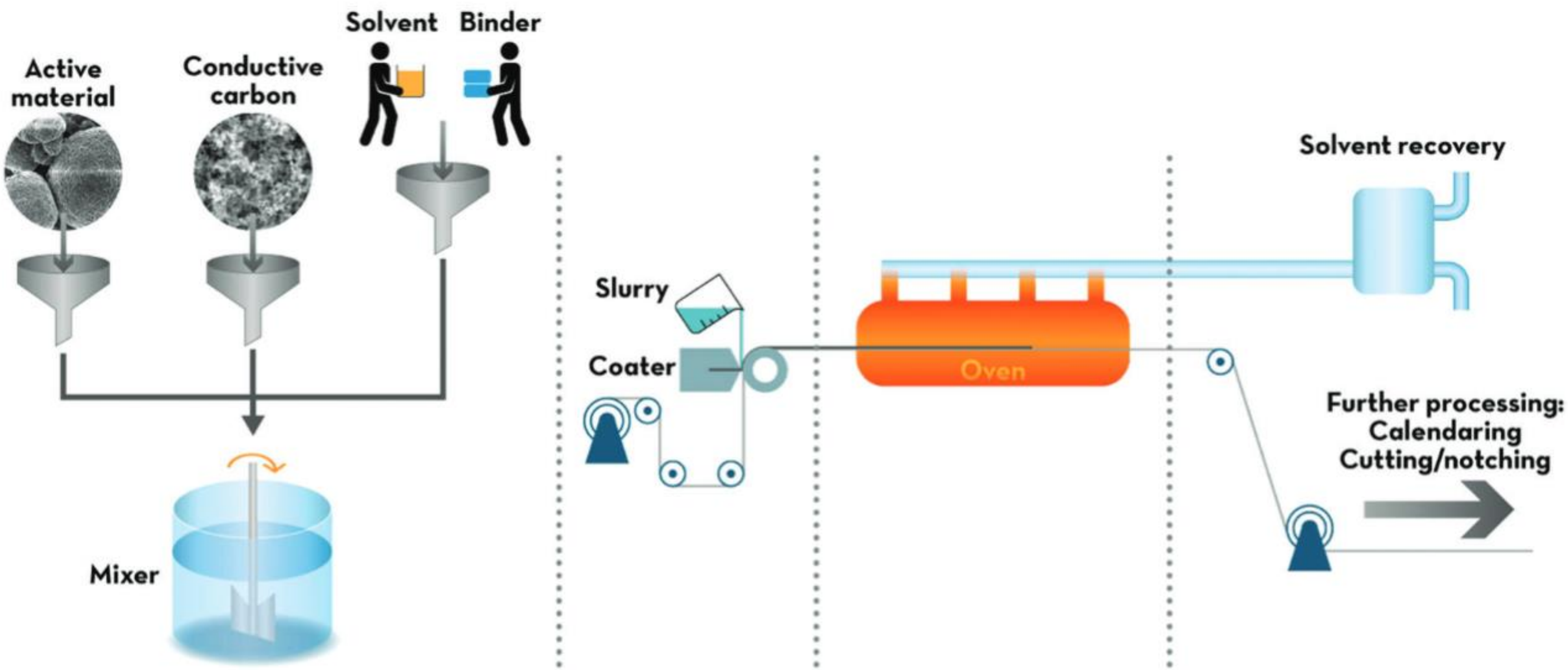
francesca.soavi@unibo.it

EES in the Waste - Water – Energy Nexus

LIB Electrode processing from NMP to Water processable binders



Solvent	Mixing	Coating	Drying	Recovery
NMP	Hazardous handling requires ventilation system and PSE	Controlled enviroment needed	Solvent vapours need to be collected to avoiding dispersion in the atmosphere	Recovery system required to recycle the expensive solvent
Water	PSE only required for handling of powders	Can be performed in air	No recovery necessary	Not needed

Today EDLC ..not so green

Separator: cellulose, PTFE,PP ca. 20-50 μm,

Electrolyte (organic): *Tetraethylammonium tetrafluoroborate* **$TEABF_4$ in** Acetonitrile, V_{MAX}=2.7 V

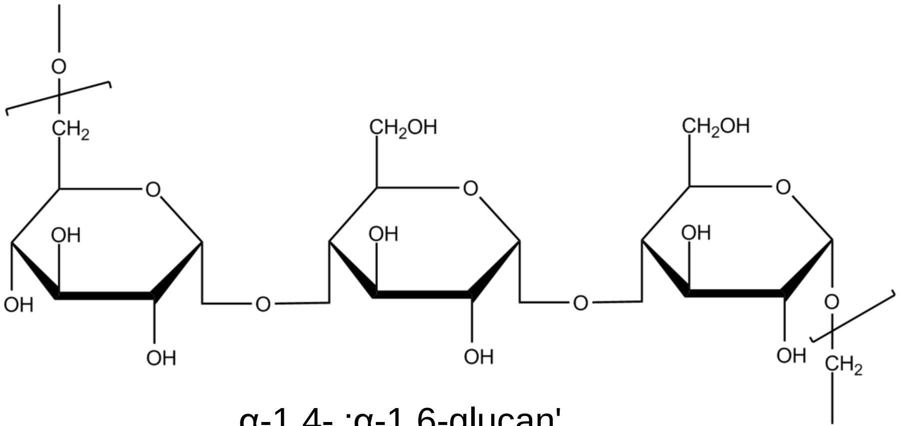
Binder: PTFE, PVDF, which require the use of *N-Methyl-2-pyrrolidone* (*NMP*) to be processed

Acetonitrile

N-metil pirrolidone (NMP)

Tetraethylammonium tetrafluoroborate

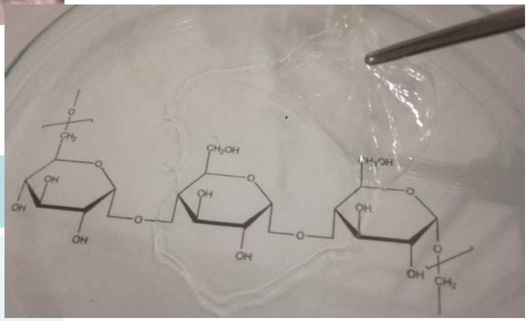
Pullulan for EES



α-1,4- ;α-1,6-glucan'

Aureobasidium pullulan fungus

Epiphyte



Chemistry	Film properties	Role in food packaging
Polysaccharide (maltotriose)	-Biodegradable -Transparent -Edible -Oil and grease resistant -Heat sealable -High water solubility -Barrier to oxygen -Stable in a wide pH range	-Coating/wrapping -Blend with other polymers to improve mechanical properties -Inner package

P.R. Vuddanda et al. European Journal of Pharmaceutical Sciences 96 (2017) 290

Pullulan for EES

Electrolyte affinity, electrochemical & chemical stability:

- Electrospun Pullan separator (Supercap)

Binding properties:

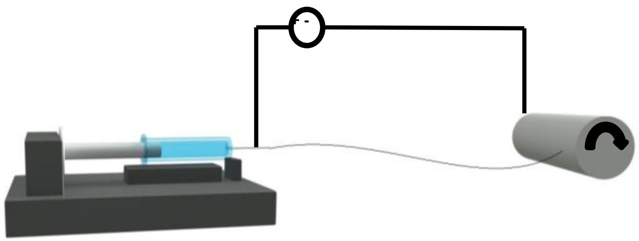
- Thick porous carbon electrodes (Supercap)
- High voltage LIB cathodes

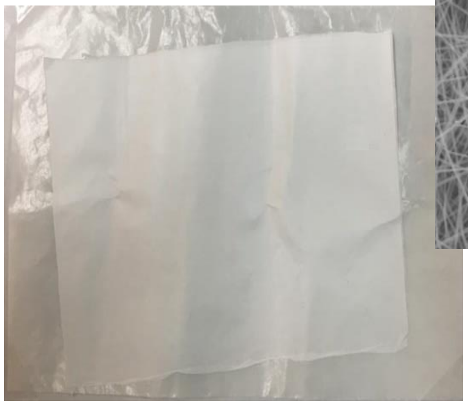
Pullulan-based separator

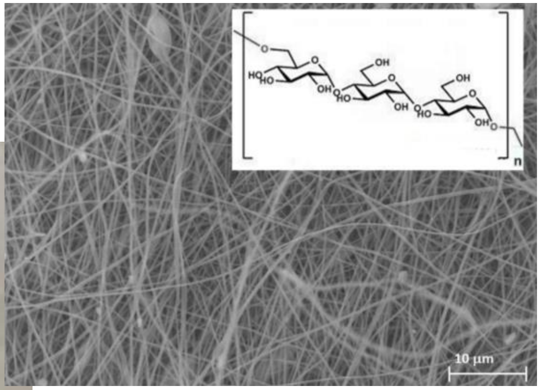
Pullulan mats prepared by electrospinning

from a 23% w/v solution of pullulan in Milli-Q water.
Spun at 18 kV at 20 cm from the collector with a flow rate of 1 mL h^{-1}.

Non woven pullulan mats thickness of $55\ \mu$m with average fiber diameter of $0.30\ \mu m$



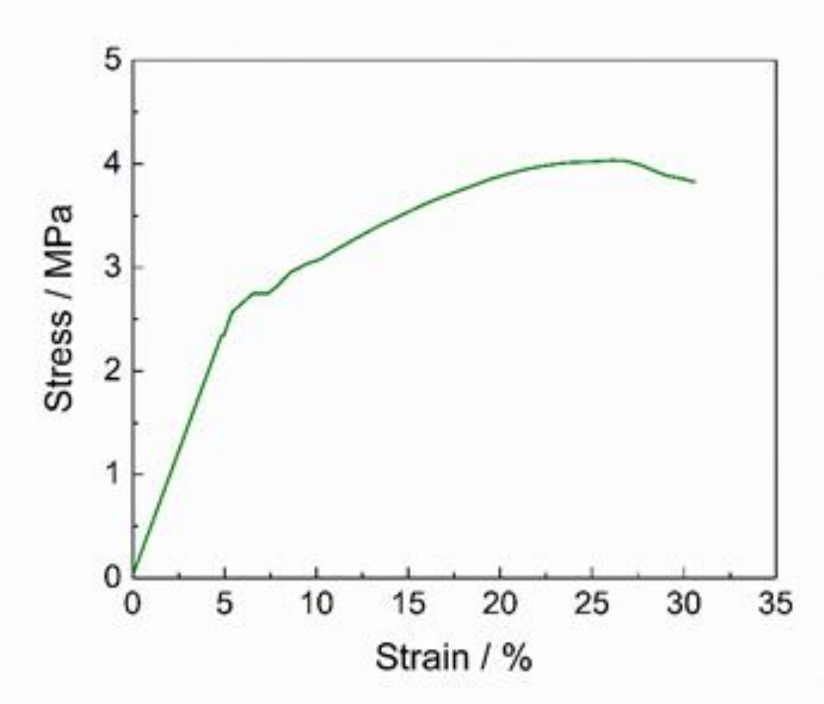




SEM at 200 kX

Pullulan electrospun separator

Tensile Stress strain

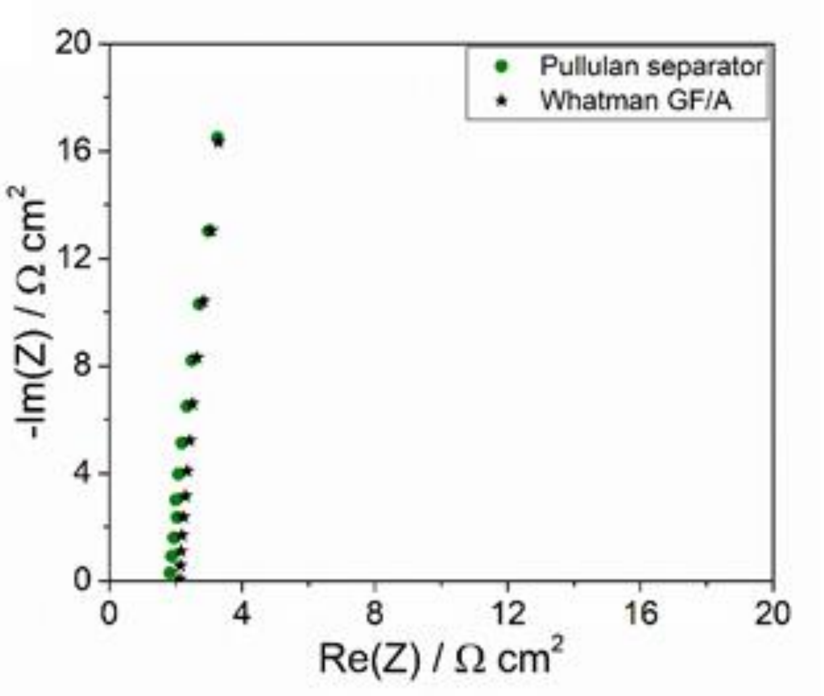


Mat elastic modulus E = 85±27 Mpa

Stress at break $\mathbf{s_b}$ **=** 3.4±0.4 MPa

Strain at break e_b = 32±9 %.

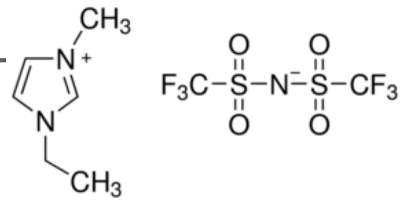
Electrochemical impedance spectroscopy



Symmetric cells with **stainless steel** blocking **electrodes** separated by the **Pullulan** membrane **and Whatman** GF/A**, (fibre glass) soaked in EMIMTFSI** (frequency range from 500 kHz to 15 kHz)

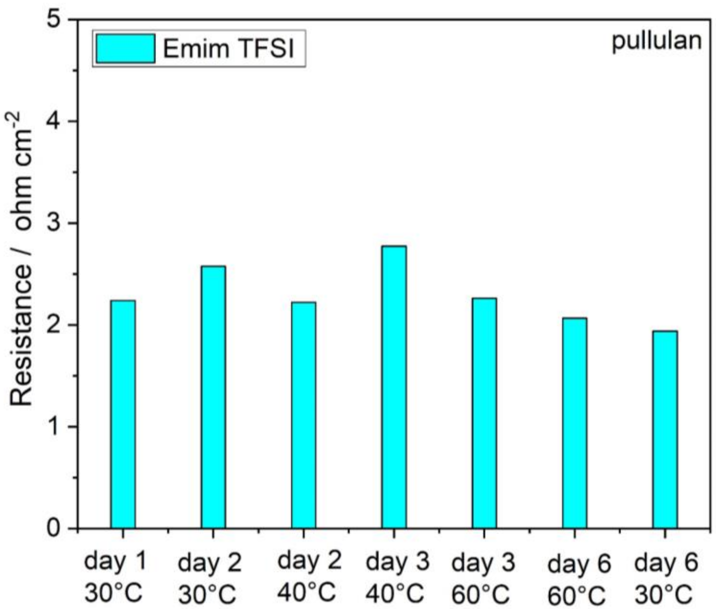
Pullulan-based separator in IL

From EIS with stainless steel blocking electrodes separated by the PU mat soaked with EmimTFSI

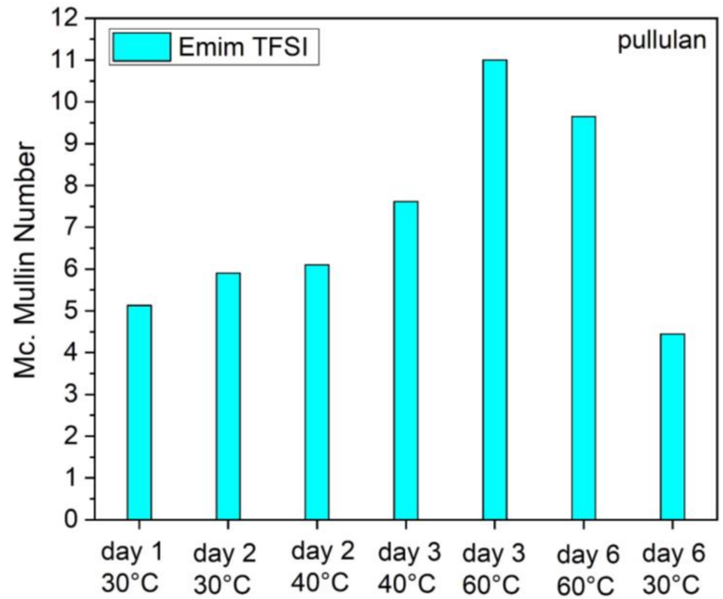


$N_M = \varrho_{eff}/\varrho_0$ *resistivity of the separator soaked in the electrolyte (ρ_{eff}) with respect to the bulk resistivity of the electrolyte solution (ρ_0)*

PU-EmimTFSI ionic Resistance



PU MacMullin number (N_M)



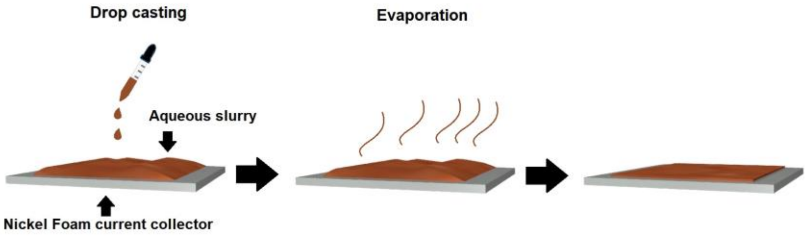
The PU mat showed low values of resistivity and MC number, constant over time

Pullulan as Electrode Binder for Supercapacitors

Evaluation of the binding efficiency in High Binder Low Mass Electrode (HBLME) and Low Binder High Mass Electrode (LBHME).
Commercial mesoporous carbon PICACTIF from PICA (BP10, BET specific surface area 1900 m^2 g^{-1})
Binder: Pullulan:Glycerol 1:1

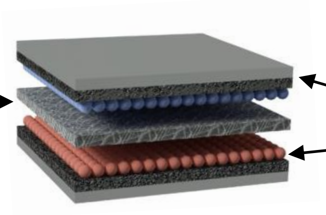
Name	Composition	Mass loading range*
HBLME	70%BP10 / 10%CB / 20%binder	3.6-4.6 mg cm^{-2}
LBHME	85%BP10 / 5%CB / 10%binder	6.3-7.5 mg cm^{-2}

*single electrodes mass loading



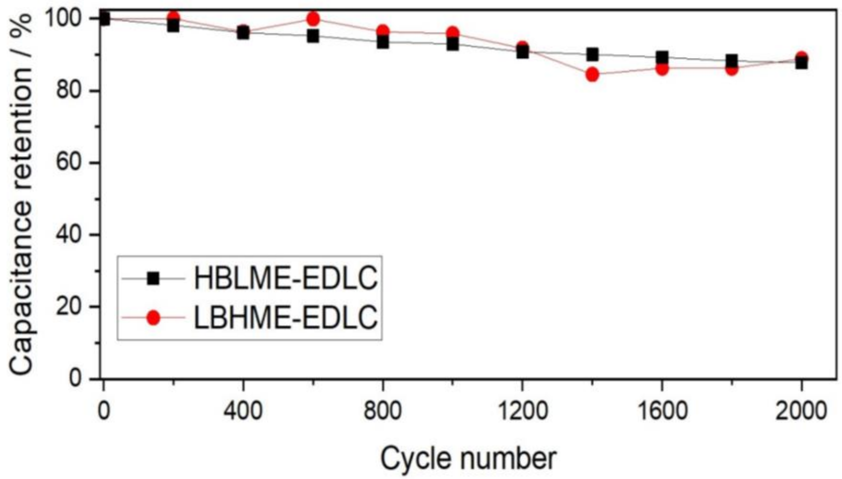
Schematic illustration of drop casting process.

PU-Supercapacitor



PU is an excellent binder even for thick electrodes working at high potentials

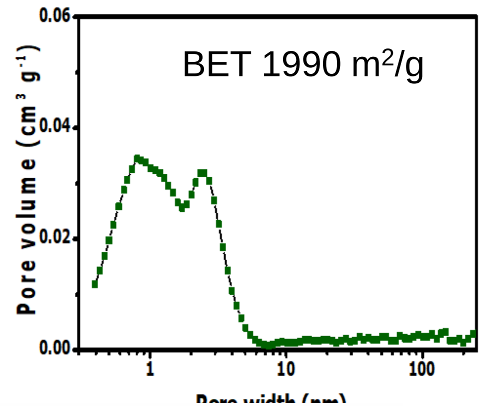
Supercpacitor GLV cycling @ 1 A/g between 0 and 3.2 V



Pullulan-based Supercapacitors

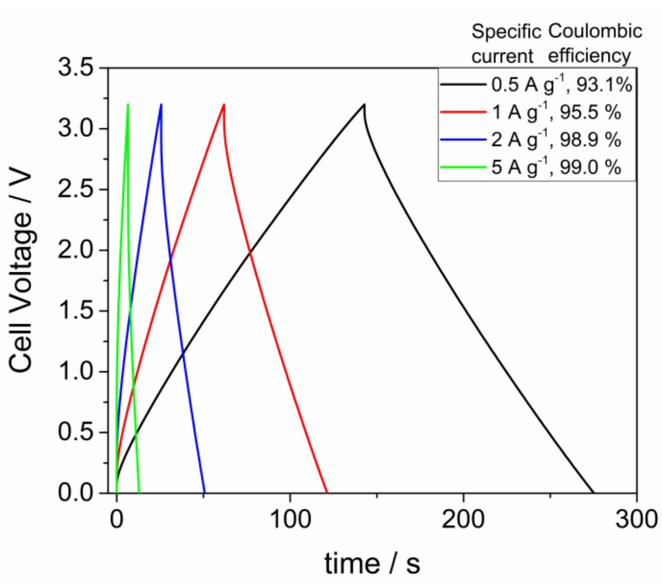
Commercial mesoporous from agriculture waste (biochar)

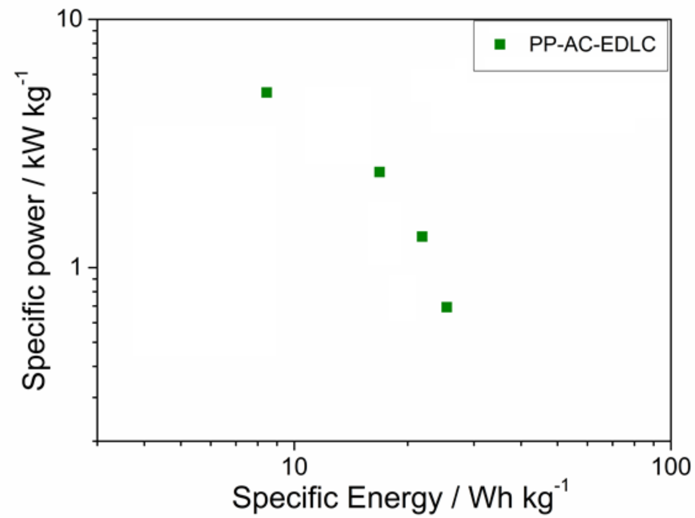
Carbon derived from the pyrolysis of bell peppers seeds at 850 °C with $KHCO_3$ activating agent



Electrode mass loading 6 - 10 mg cm^{-2}

Electrode composition:70% AC-10 % acetylene balck- 20 % PU
Electrolyte: EmimTFSI – Separator: Electrospun PU





Specific capacitance	*27 F g^{-1}*
Specific power	*7 kW kg^{-1} at 5 A g^{-1}*
Specific energy	*25 Wh kg^{-1} at 0.25 A g^{-1}*

Stable over more than 2000 cycles

Conclusions

- Pullulan can be used to design the major components (binder and separator) of green supercapacitors by sustainable, water based manufacturing procedures (electrospinning).

- The electrode and membrane processes that we propose represent environmentally improved and safer routes that can substitute the conventional manufacturing of fluorinated polymers based on the use of the toxic solvent N-Methyl-pyrrolidone.

- Pullulan can be exploited for the aqueous processing of NMC cathodes with comparable performance to PVdF-based electrodes

- LIB cathode preparation procedure should be further optimized to achieve full exploitation of the active material

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