FeBDC MOF thin layer for the passivation of silicon anodes for Lithium-ion batteries

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FeBDC metal organic framework (MOF) thin layers for the passivation of Si anode in Li-ion batteries

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Introduction

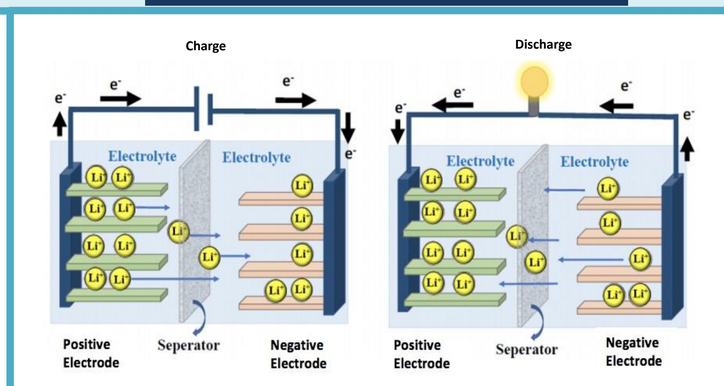
Silicon is a very attractive and promising material to replace carbon for negative electrodes in lithium-ion batteries (LIBs) because of its higher theoretical storage capacity (10 times superior to that of carbon). Its high theoretical capacity is however counter balanced by two major drawbacks: huge volume changes during lithiation/ delithiation processes inducing electrode structural damaging and the formation of an instable passivation layer (called Solid Electrolyte Interphase, SEI) resulting from the electrochemical decomposition of the electrolyte. The realization of an artificial passivation layer – insulating but ion conductive – should avoid the capacity fading associated to the SEI formation. Because of their porosity and their – generally – insulating character, MOFs are very attractive material for the realization of such an artificial passivating layer.

In this work, we developed synthesis procedures allowing for the growth of Fe-BDC MOF thin layers on Si surfaces and investigated the electrochemical behavior of Si-MOF hybrid electrodes in cycling conditions.

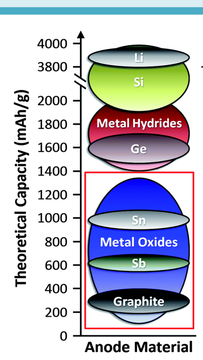
Our results reveal improved electrochemical performances in presence of the FeBDC passivating layer. Higher coulombic efficiencies (superior to 99.7%) and longer capacity retentions are observed compared to non-passivated electrodes.

Backgrounds

Li-ion batteries principle



Anode material for Lithium-ion batteries



[1]

Silicon

Advantages:
- High capacity (Carbon x 10)
- Safe, abundant
- Environment friendly

Major drawbacks:
- Volume expansion (300%)
- An instable passivating layer (SEI: Solid Electrolyte Interphase)
- Low conductivity

Volume expansion > SEI damaging > Continuous SEI growth

- Consumption of Li-ions
- Increase of the lithium diffusion path

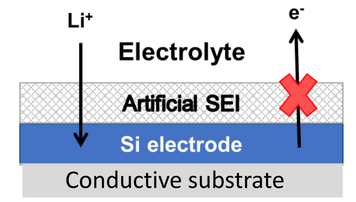
Fading of the electrochemical performances (efficiency and capacity loss) during cycling

[1] Shimotake, H., Progress in batteries and solar cells. JEC Press: 1990.

[2] A. Wang *et al.* *(2018) Computational Materials*, *4*(1), 1-26.

Objective

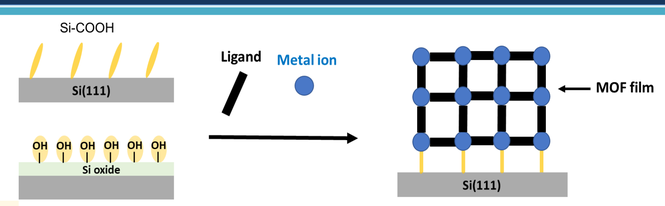
Proposed approach: Passivation of the Si electrode by an **insulating** but **ion conductive artificial SEI layer**



MOFs => good candidates:
- Open porosity, electronic insulators

Growth strategy of MOFs on Si surfaces

Synthesis



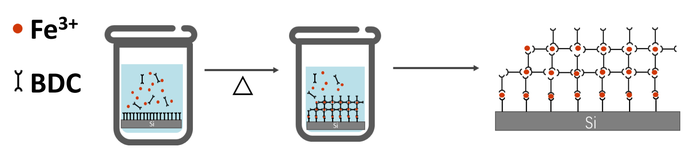
Tunable surface chemistry
Interface compatible with a wide range of MOF synthesis conditions
- *Robust surface anchoring*
- *Great chemical and thermal stability*

Various silicon subsrates

Synthesis

Precursors : Fe^{3+} + Benzene 1, 4-dicarboxylic acid (BDC)

Organic ligand

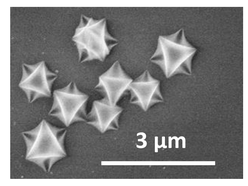


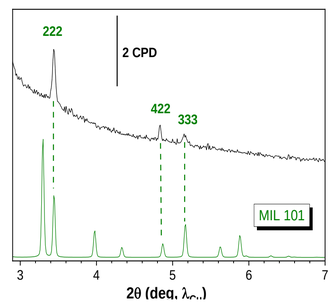
In nominal solution

24H **Synthesis conditions** : metal excess C_{Fe} = 25 mM = 2 C_{BDC}

No HCl /H_2O addition

low density of 3D octahedral MIL-101 crystallites





Effect of HCl / H20 Addition

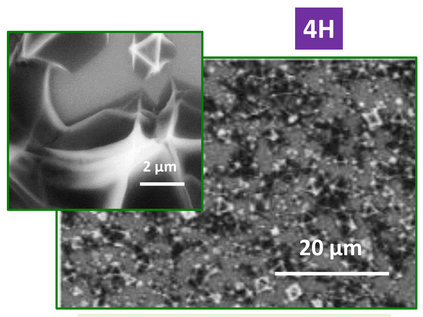
Growth of MOF layers

Synthesis conditions
C_{Fe} = 25 mM = 2 C_{BDC}
T = 90°C

+ 1ml 1M HCl

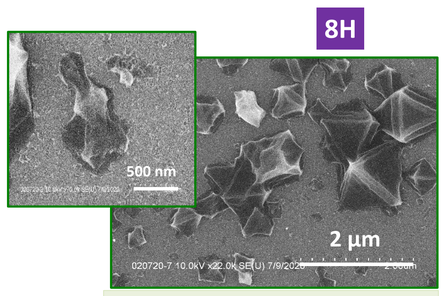
C_{HCl} = 10 mM C_{H_2O} = 0.5 M

4H



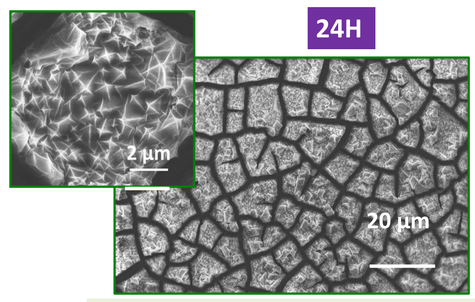
discontinuous layer

8H

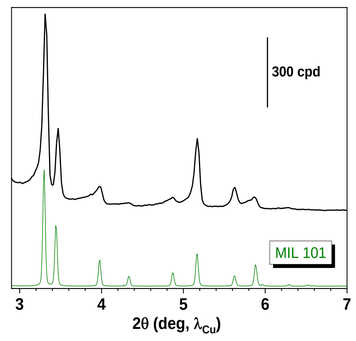


Thin layer +
3D crystallites (µm size)

24H

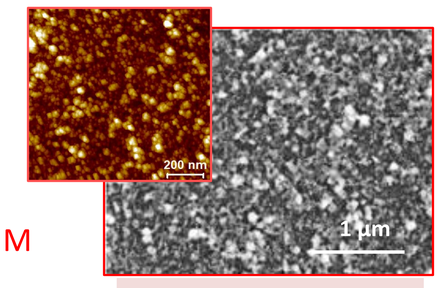


Polycrystalline MIL 101 layer
(~1 µm thick)

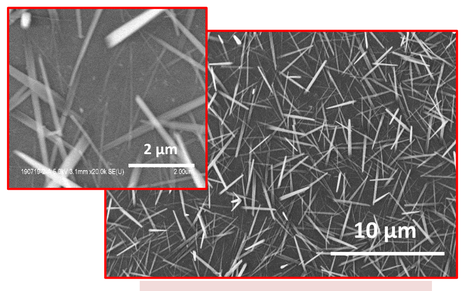


+ 5ml 1M HCl

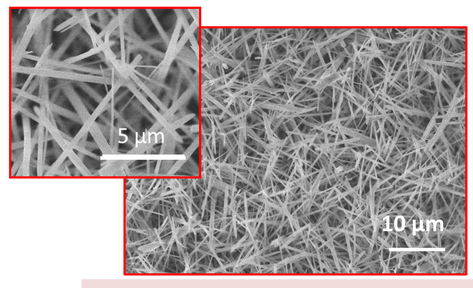
C_{HCl} = 50 mM C_{H_2O} = 2.7 M



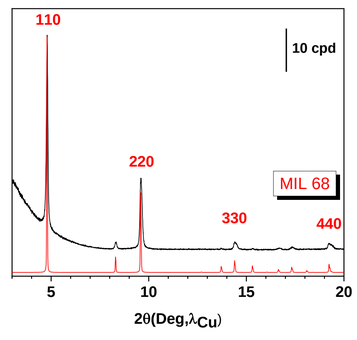
Dense granular thin layer



Thin layer + needles



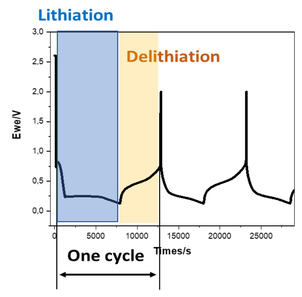
MIL 68 needles (surface growth)



Amorphous-Si/MOF hybrid electrodes

Applications

Electrochemical conditions
Galvanostatic cycling with potential limitation
(no lithiation of the c-Si substrate)



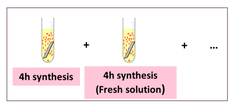
CE Current collector
lithium
Separator + electrolyte
a-Si electrode
WE Conductive substrate

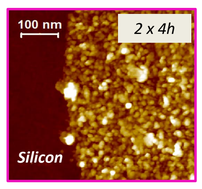
Structure of the cell

Coulombic efficiency (CE) = $Q_{delithiation}/Q_{lithiation}$

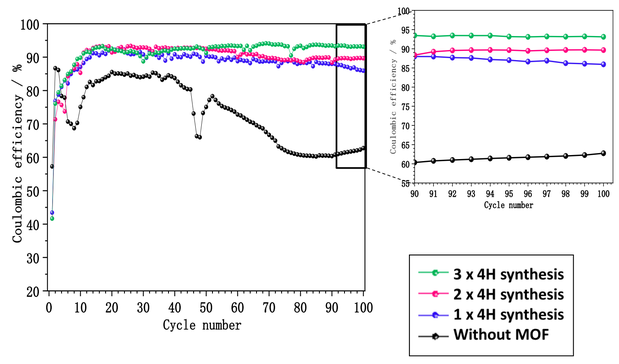
Coulombic efficiency and Capacity retention

Synthesis procedure





FeBDC layer thickness ~ 8 nm

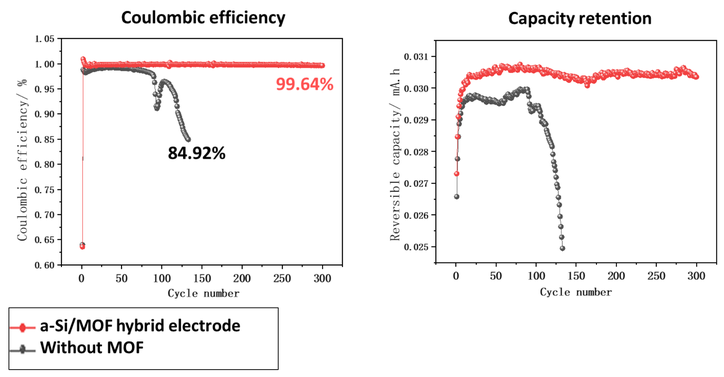


	a-Si without MOF	1 x 4H	2 x 4H	3 x 4H
$CE_{average}$ (90 – 100 cycles)	61.75 %	86.8 %	89.62%	93.25%

Improved long-term Coulombic efficiency

Recent results

New cell design



Improved Coulombic efficiency (> 99%)
Improved Capacity retention
(Long term cycling > 300 cycles)

Conclusions

- Development of synthesis procedures to get dense **FeBDC MOF thin layers** on c-Si (< 10 nm)
- Successfull transfer to the formation of **FeBDC MOF thin layers** on a-Si electrodes
- **Efficient passivation** of the a-Si electrode: improvement of the **Coulombic efficiency & Capacity retention**