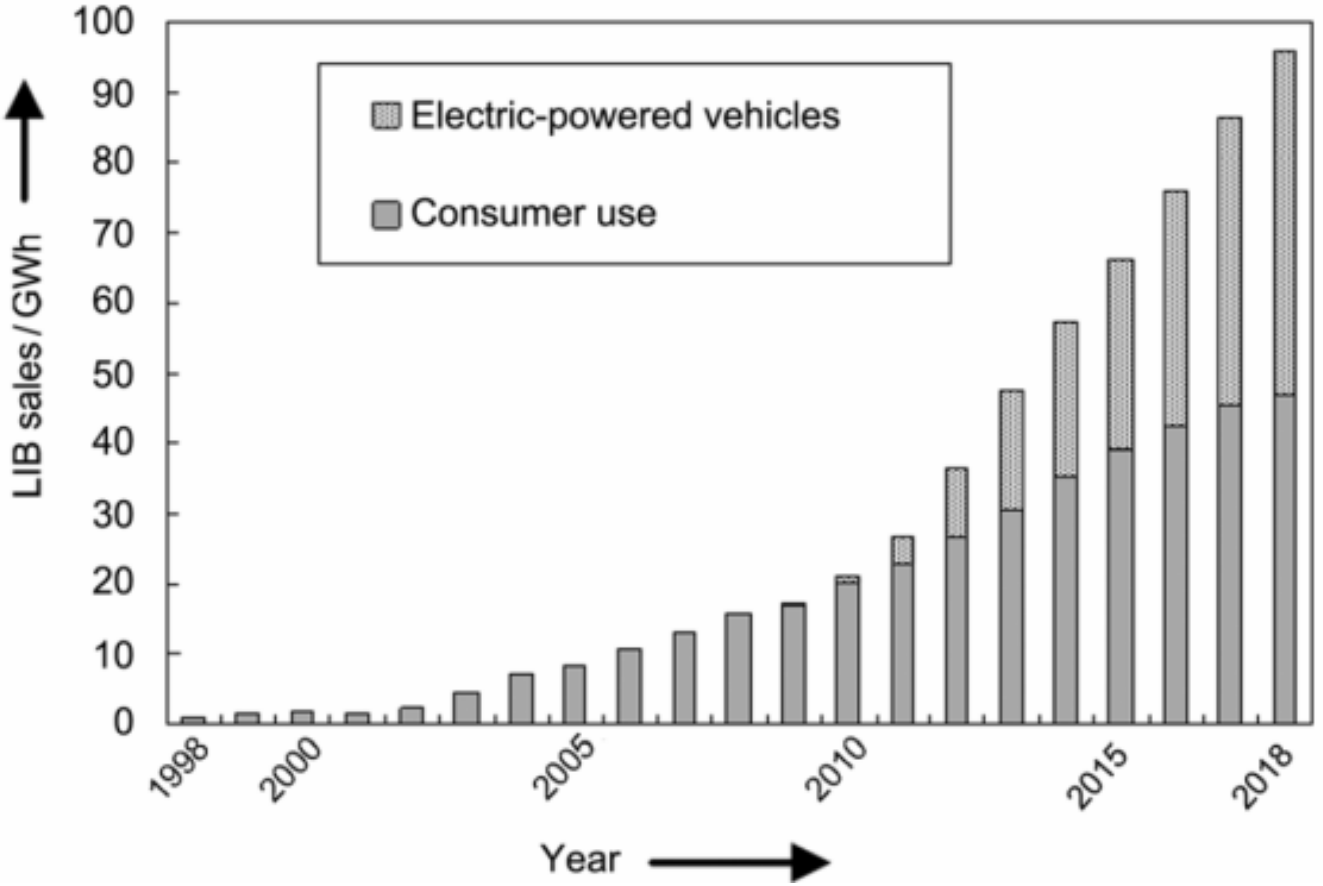
Use of paper-making techniques for the production of Li-ion paper-batteries

LGP2 - Grenoble (France) : Lara JABBOUR, Davide BENEVENTI, Didier CHAUSSY

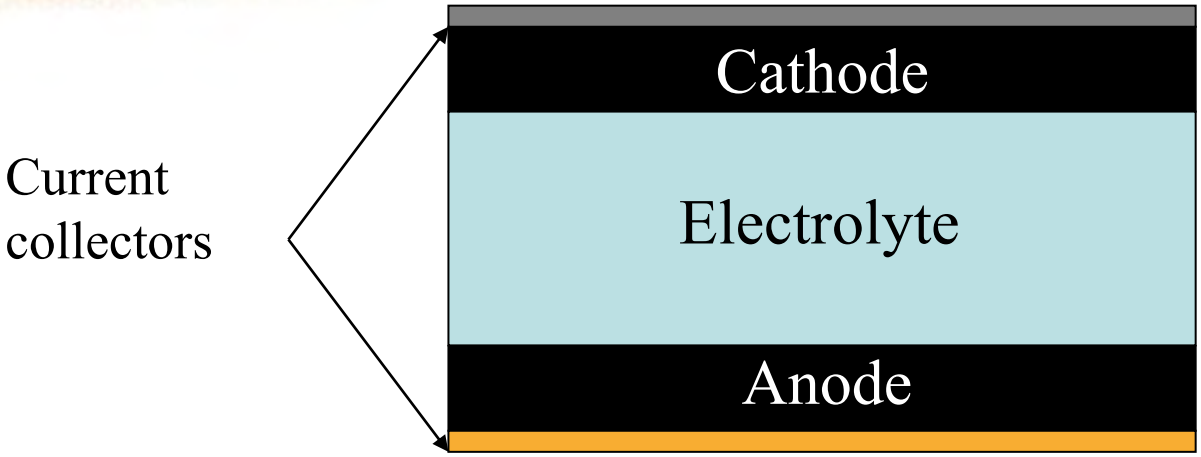
Politecnico di Torino (Italy): Matteo DESTRO, Claudio GERBALDI, Nerino PENAZZI

Why Li-ion batteries ?



A. Yoshino, The Birth of the Lithium-Ion Battery, Angewandte Chemie International Edition. 51 (2012) 2-5.

What is a battery ?



The cell consists of three major components:

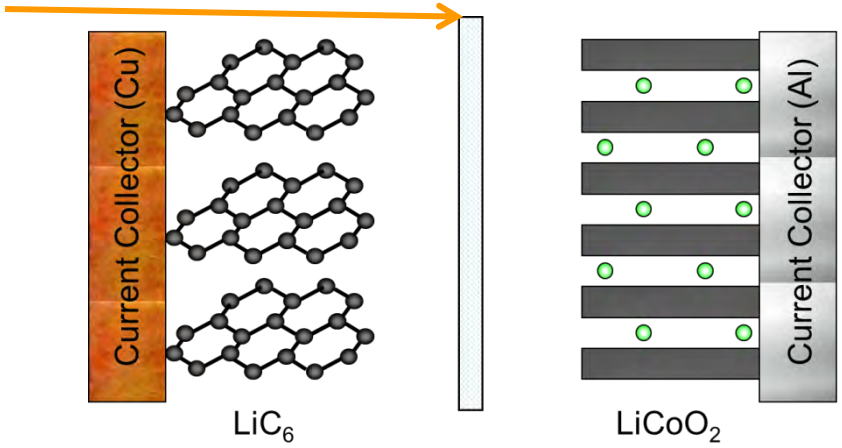
1. The anode or negative electrode, which gives up electrons to the external circuit and is oxidized during the electrochemical reaction.

2. The cathode or positive electrode, which accepts electrons from the external circuit and is reduced during the electrochemical reaction.

3. The electrolyte, which provides the medium for transfer of charge, as ions, inside the cell between the anode and cathode.

Li-ion cell

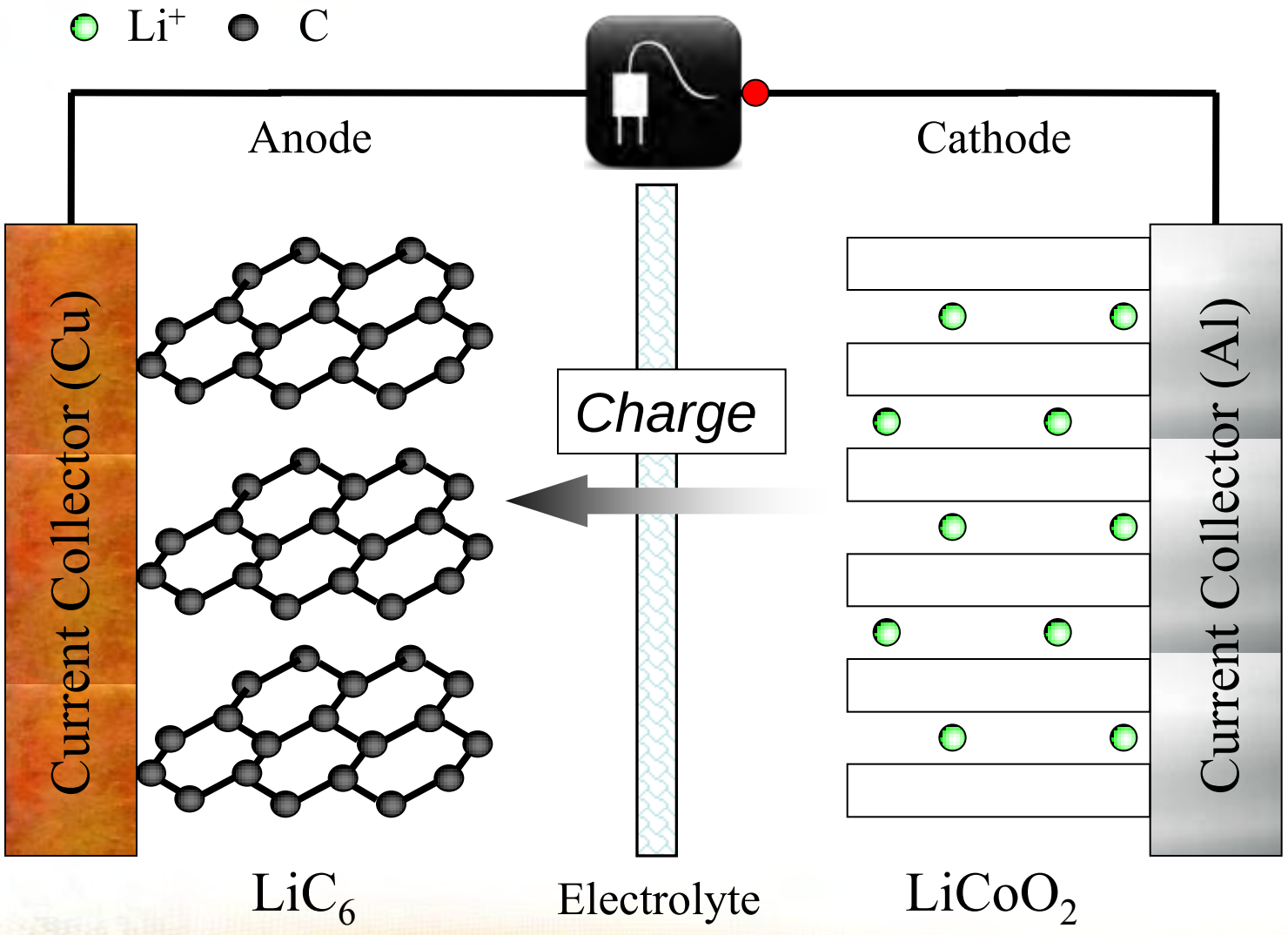
Micropourous
PE PP separator



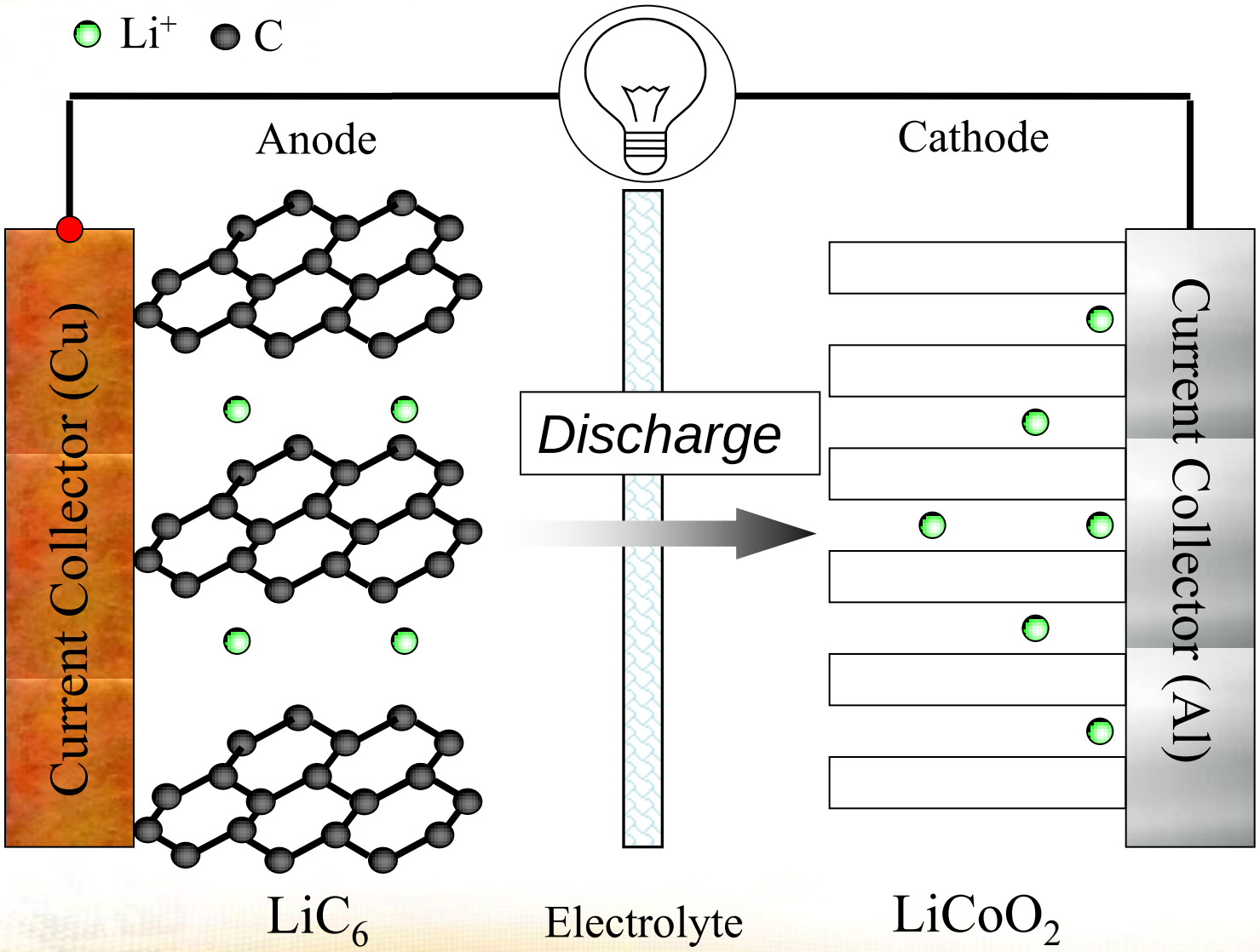
Electrode slurry preparation
Active material (e.g. $LiCoO_4$, GP) + binder (e.g. PVdF)+ conductivity enhancer (e.g. CB)+organic solvent (e.g. NMP))

→ Coating → Solvent evaporation

Li-ion cell


Li+
C
Anode
Cathode
Current Collector (Cu)
Charge
Current Collector (Al)
LiC6
Electrolyte
LiCoO2

Li-ion cell


Li+
C
Anode
Cathode
Current Collector (Cu)
Discharge
Current Collector (Al)
LiC6
Electrolyte
LiCoO2

Li-ion cell

Drawbacks

- High cost and toxic active materials (e.g. $LiCoO_2$)
- High cost and not easily disposable polymer binders (e.g. PVdF) and separators
- Metal foils as electrode substrate. Increase of the cell cost and weight
- High cost and high environmental impact process based on organic solvents(e.g. NMP)

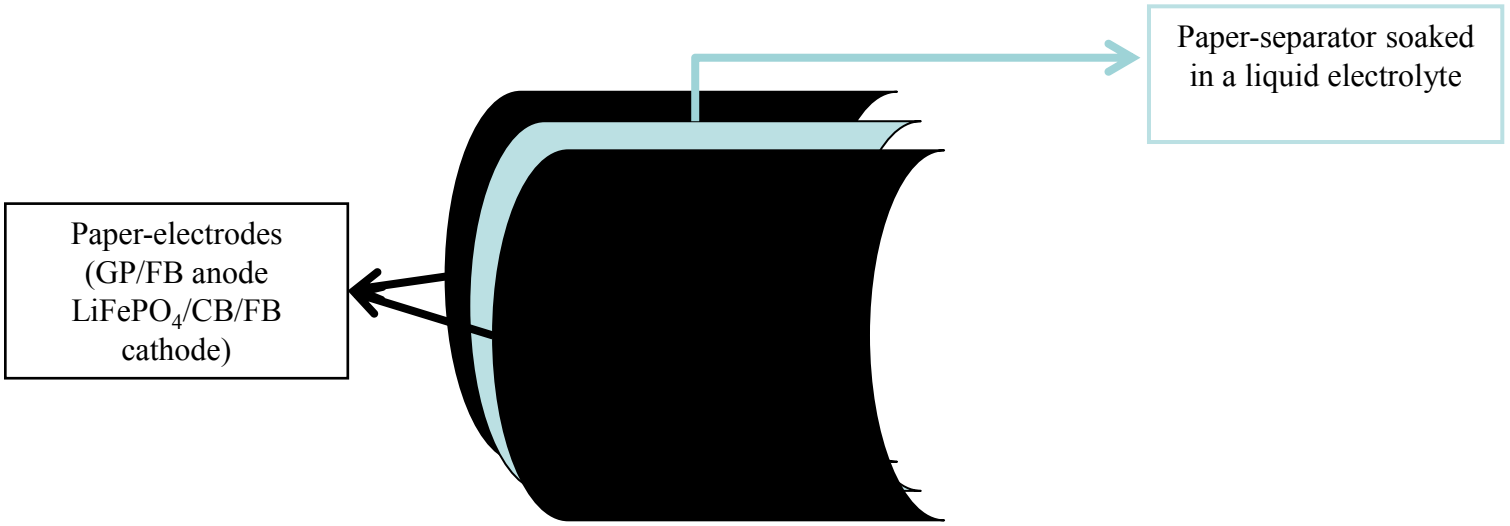
Li-ion cell

Challenges

- Reduce the production and device cost
- Identify environmentally friendly materials and production processes
- Develop easily up-scalable & recyclables devices

Objective

Development of low-cost and environmental friendly Li-ion paper-cells



- Low cost and easily recyclables cellulose fibers as electrode binder and common paper as separator
- Quick aqueous filtration process easily up-scalable
- Eco friendly active materials

Materials & Methods

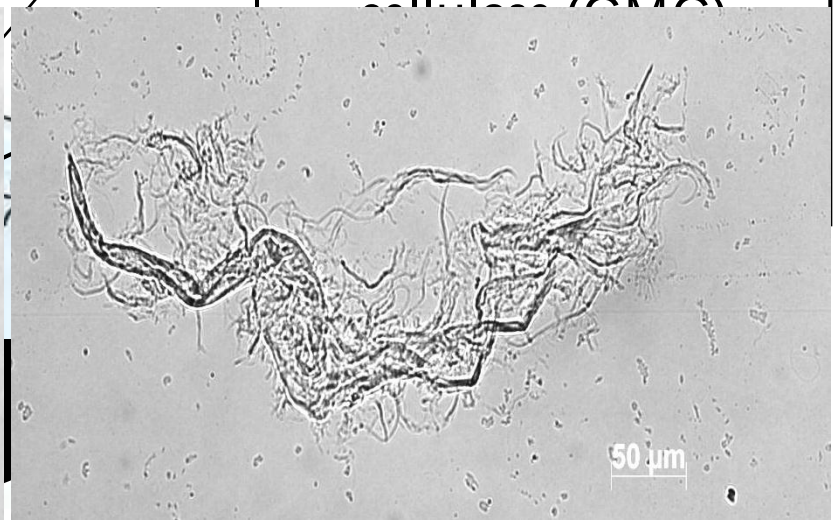
Paper-anode formulation

Cellulose fibers (FB)
(Eucalyptus 96°SR)

Graphite (GP)
(particle size <20 µm)

H_2O

Sodium carboxymethyl



Sample	Solid phase weight fractions in the forming slurry	Forming additives weight fractions	Consistency of the forming slurry (%)	FB °SR
Anode [1,2]	90% GP and 10% FB	0.0001% CMC	0.1	96

(1) "Aqueous processing of cellulose based paper-anodes for flexible Li-ion batteries", L. Jabbour, M. Destro, C. Gerbaldi, D. Chaussy, N. Penazzi and D. Beneventi, J. Mater. Chem. 22 (2012) 3227-3233.
(2) "Procédé de préparation d'électrodes flexibles auto-supportées", L. Jabbour, D. Chaussy, D. Beneventi , M. Destro, S. Bodoardo ,C. Gerbaldi and N. Penazzi, Patent Submission number 1000125997.

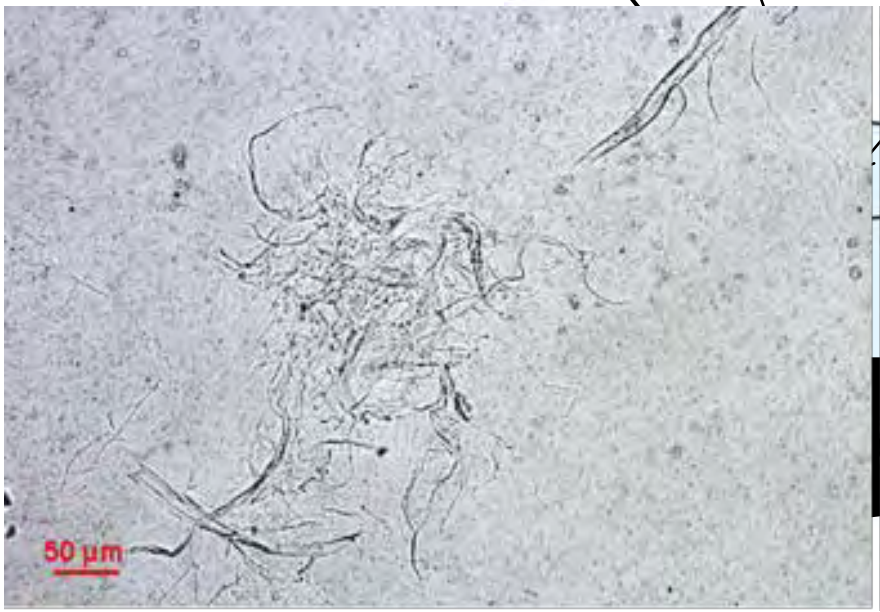
Paper-cathode formulation

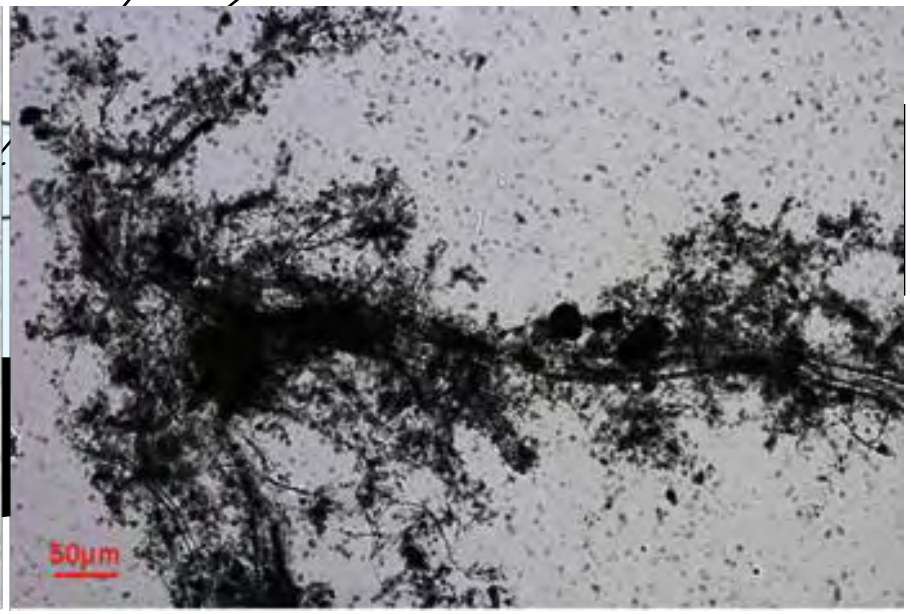
$LiFePO_4$ (particle size <100 nm)

H_2O

Carbon black (CB) (particle size <50 nm)

$Al_2(SO_4)_3 \cdot 14H_2O$ (Alum)

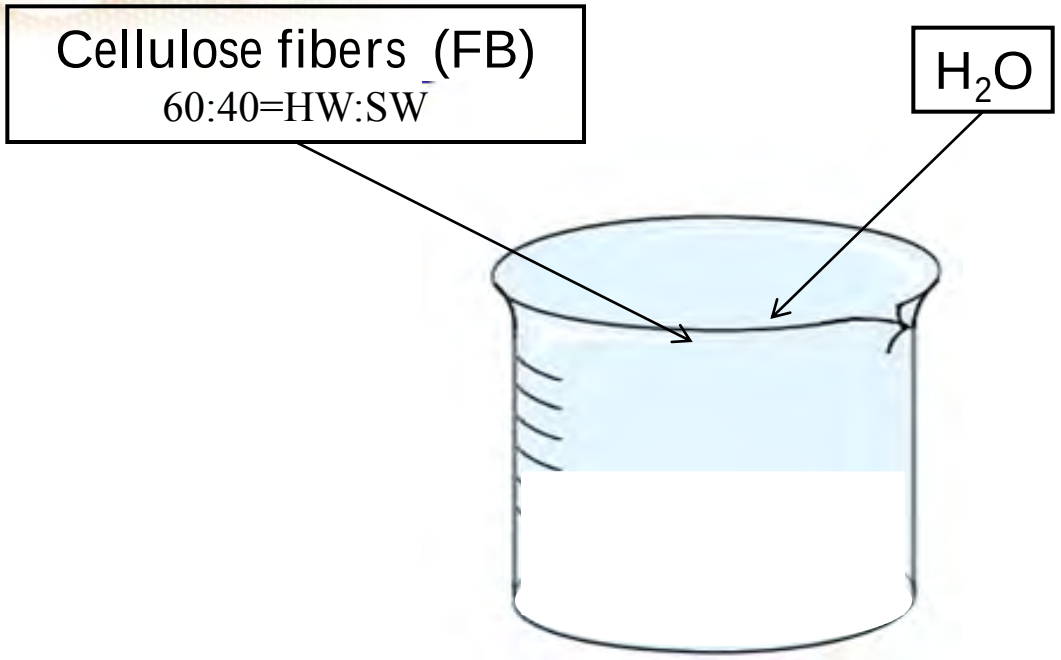




Sample	Solid phase weight fractions in the forming slurry	Forming additives weight fractions	Consistency of the forming slurry (%)	FB °SR
Cathode (2)	60% $LiFePO_4$ 24% CB and 16% FB	0.01% of CMC and 0.008% of Alum	0.16	96

(2) "Procédé de préparation d'électrodes flexibles auto-supportées", L. Jabbour, D. Chaussy, D. Beneventi , M. Destro, S. Bodoardo ,C. Gerbaldi and N. Penazzi, Patent Submission number 1000125997.

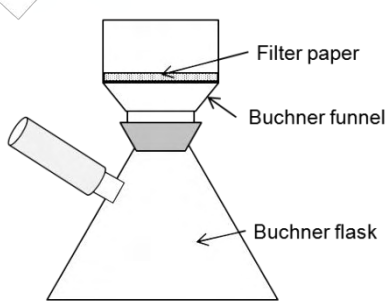
Paper-separator formulation



Sample	Solid phase weight fractions in the forming slurry	Forming additives weight fractions	Consistency of the forming slurry (%)	FB °SR
Separator	100% FB (60:40=HW:SW)	none	0.2	35

Paper-electrode preparation

Filtering

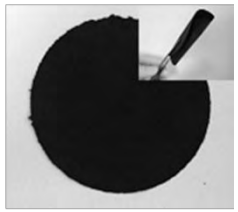


(a)

Drying

in vacuum for 10 minutes at 90°C

(b)



(c)

Paper-separator preparation

Filtering

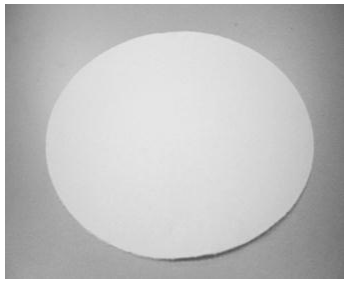
Using a sheet former according to ISO 5269/2

(a)

Drying

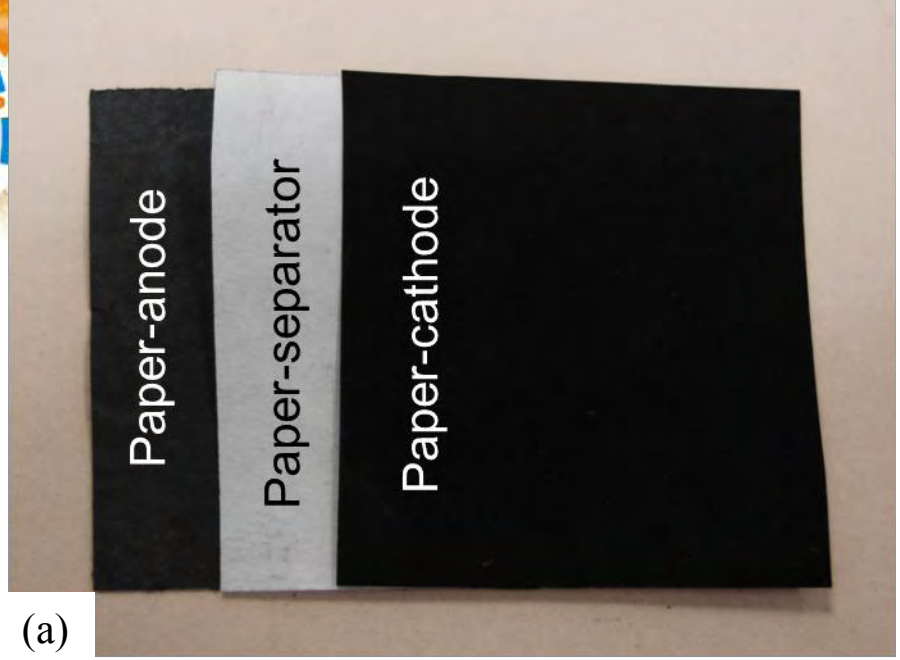
in vacuum for 10 minutes at 90 C

(b)



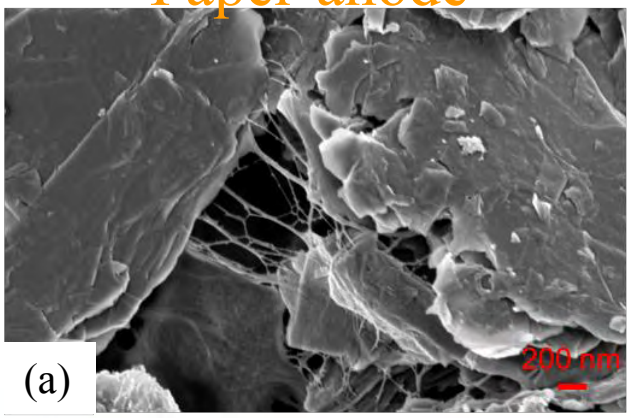
(c)

Characterizations

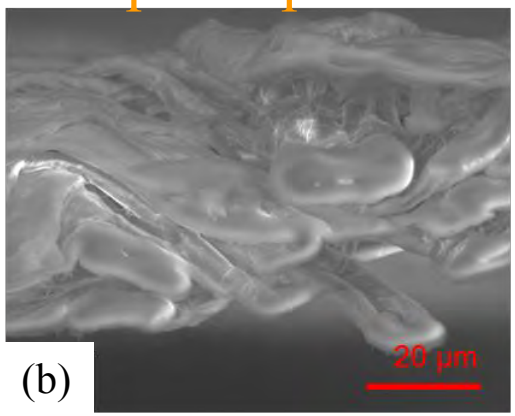


FESEM and SEM Images

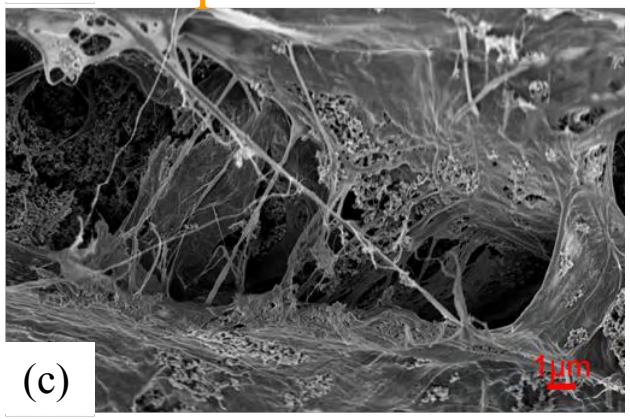
Paper-anode



Paper-separator



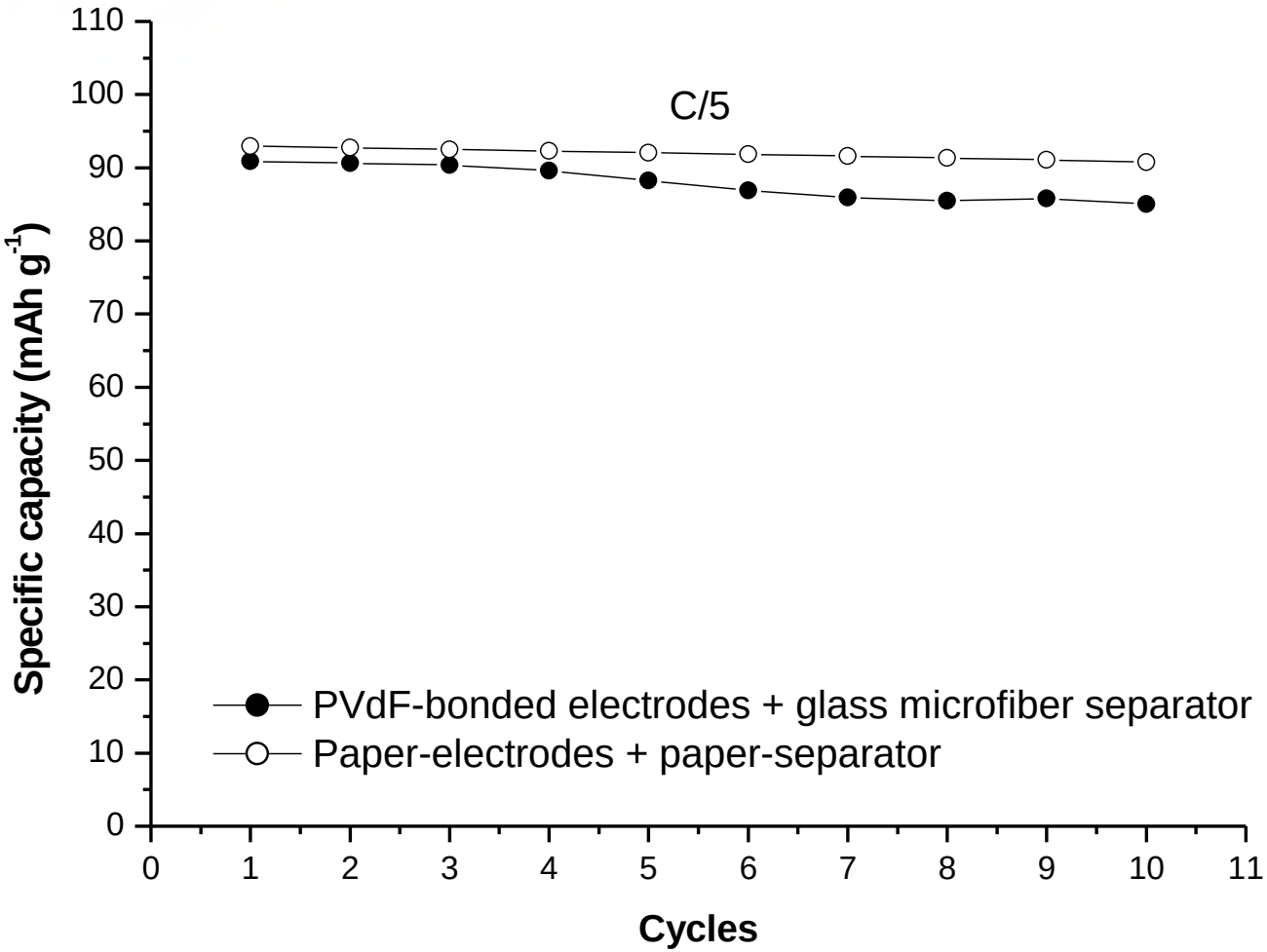
Paper-cathode



Sample	Grammage ($g\ m^{-2}$)	Thickness (µm)	Young Modulus (MPa)	Electron conductivity ($S\ m^{-1}$)
Cathode	68 ± 3	282 ± 33	90 ± 9	1.4 ± 0.6
Anode	69 ± 5	126 ± 7	101 ± 19	162 ± 16
Separator	59 ± 2	106 ± 3	781 ± 11	-

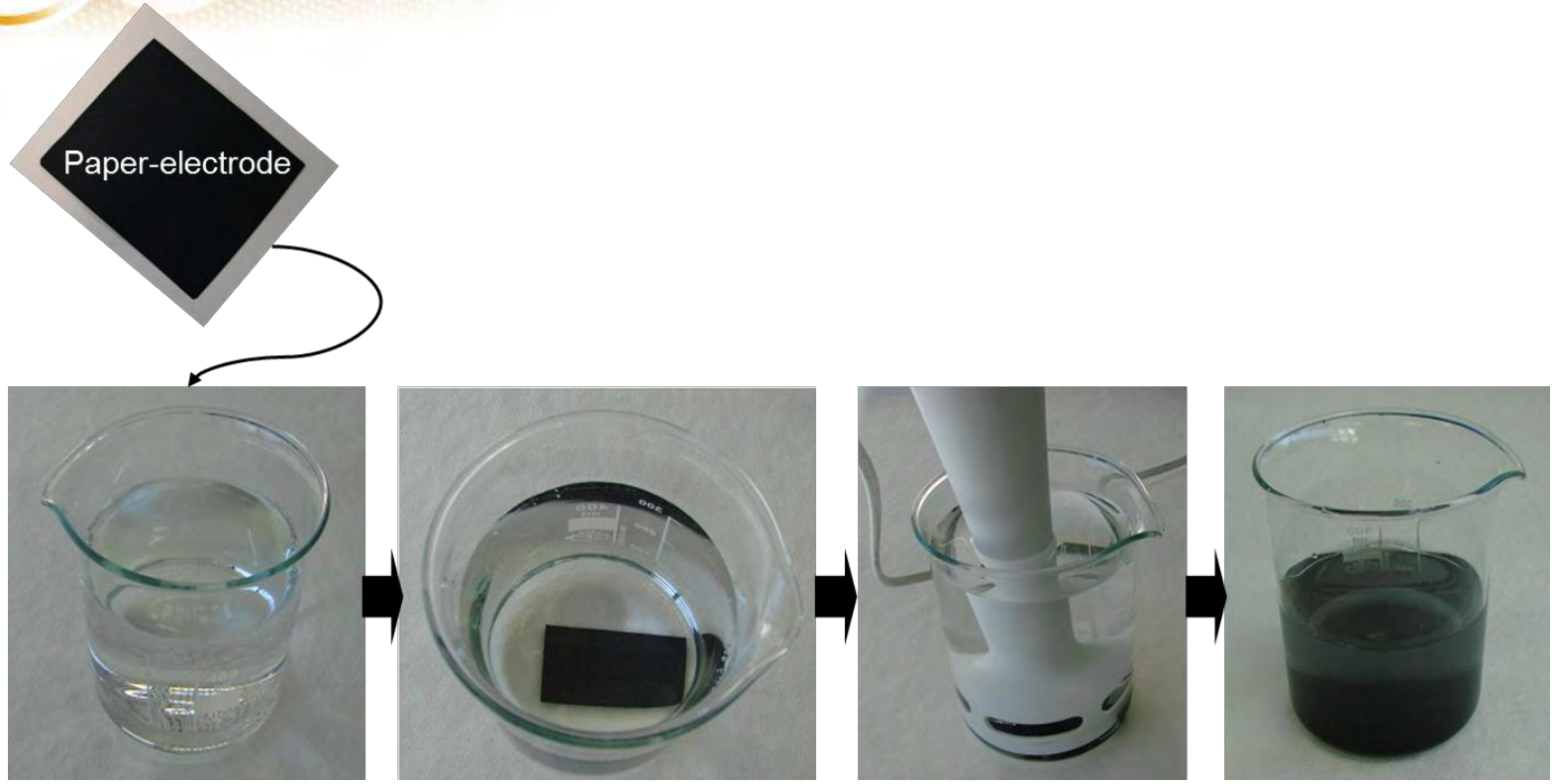
Paper Cell Ą ~300 $g\ m^{-2}$ and ~700 µm

Electrochemical Characterization



Liquid electrolyte Ą 1 mol L^{-1} $LiPF_6$ solution in a 1: 1 mixture of EC and DEC

Recyclability



Conclusions

- A completely cellulose based paper-cell was obtained, using FBs as electrode binder and paper sheets as separator
- Water-based and easily up-scalable production process. No organic solvents or synthetic polymer binders involved
- The paper-cell showed good electrochemical performances, comparables with standard PVdF-bonded electrode cells
- Paper-cell components are easily redispersable in water

Thank you