Vanadium redox flow battery for smart grid application: Nano-structured carbon-based electrode materials

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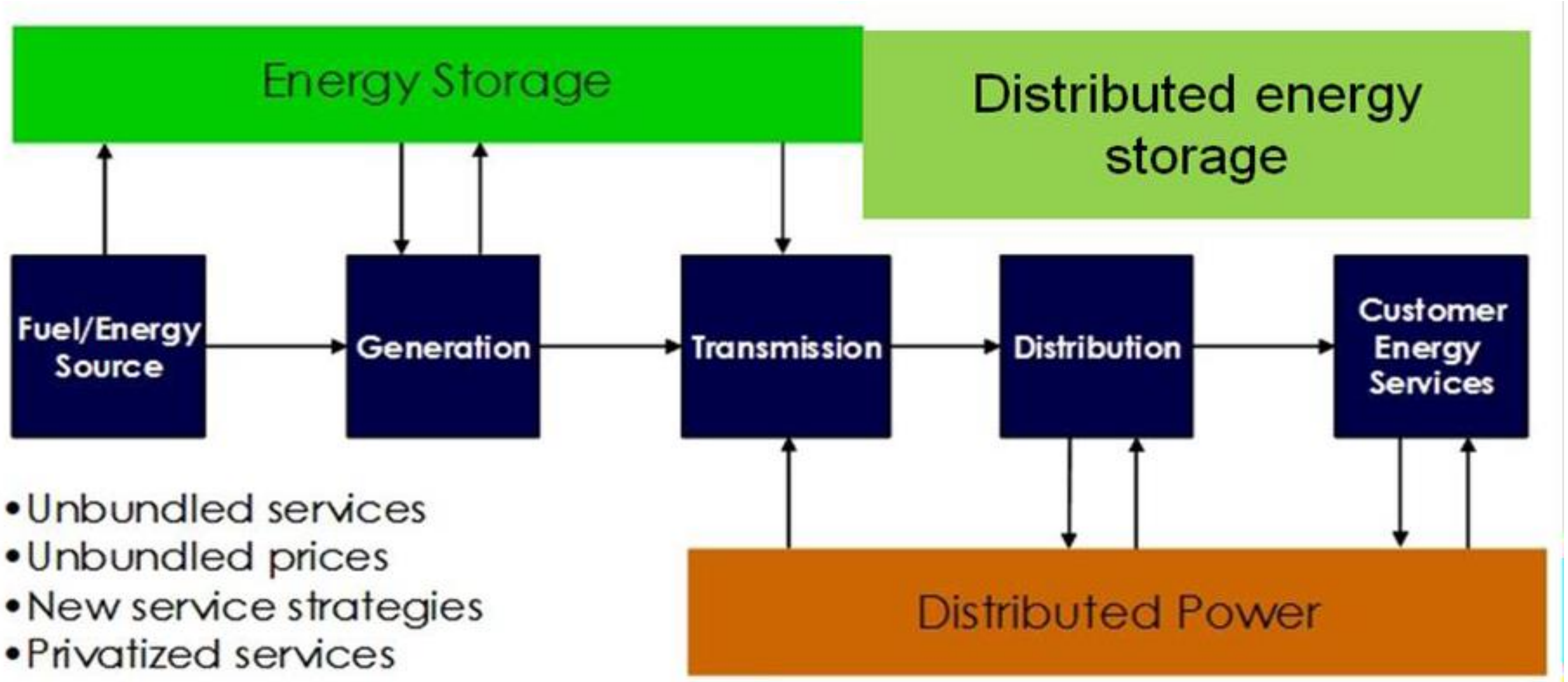
MOTIVATION

EU 2050 ENERGY ROAD MAP:

- 99% renewal integration
- Low- carbon energy system



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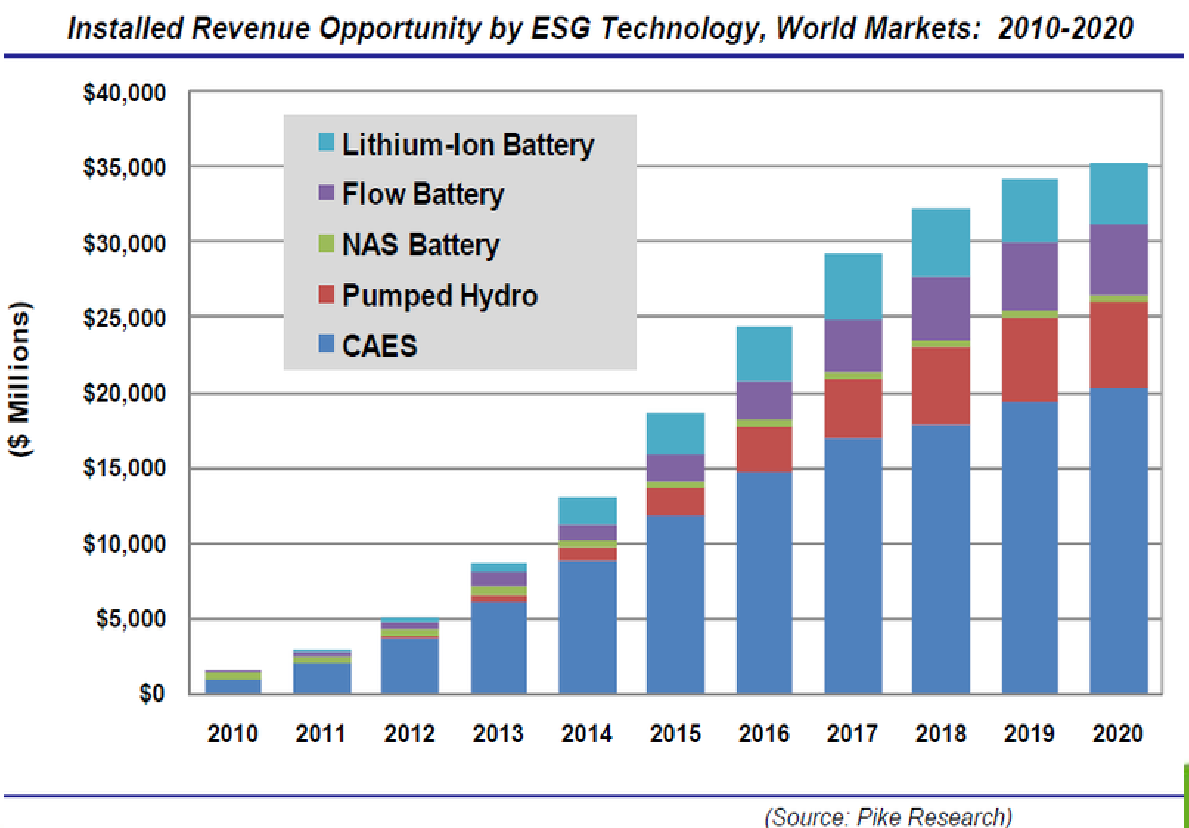
Distributed renewal energy source integration

ELECTROCHEMICAL ENERGY STORAGE: VANADIUM REDOX FLOW BATTERIES

XARXA DE REFERENCIA EN MATERIALS AVANÇATS PER A L'ENERGIA

- EES is not dependent site and high capital cost (CAE and PHS)
- Power and energy are decoupled : Flexible and modularity design (unlike Li-ion or NAS batteries) making it suitable for many diverse application



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MOTIVATION

Why vanadium redox flow battery such as energy store device?

- EES is not dependent site
- Power and energy are decoupled
- Low maintenances cost
- High voltage efficiency **>85% total efficiency**
- Recharged by simply replacing the electrolyte
- Limited environmental impact when compared with lead-acid
- Fast response time
- Low self-discharge

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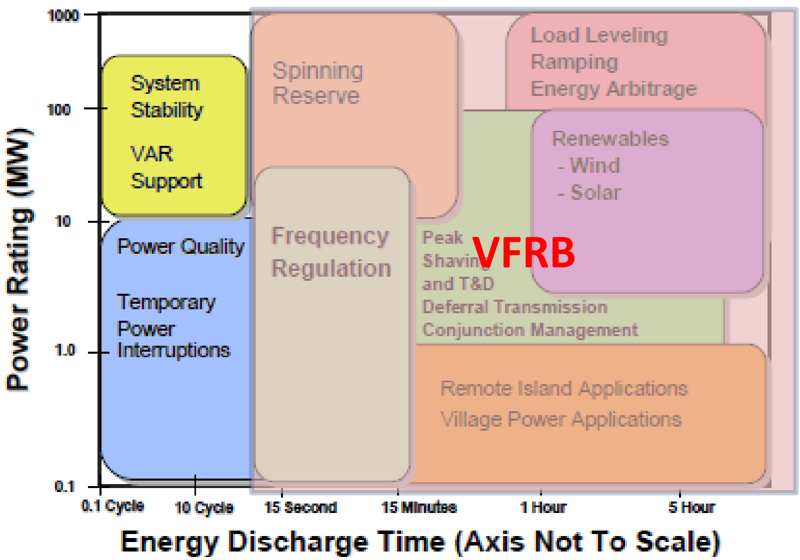
COST (EASE-EERA roadmap)

Energy cost 120 €/kWh

Power cost 300 €/kW

2 MW / 4 h 245 m^2



Source: Electric Power Research Institute

Figure 1-1
Overview of Energy Storage Use Cases

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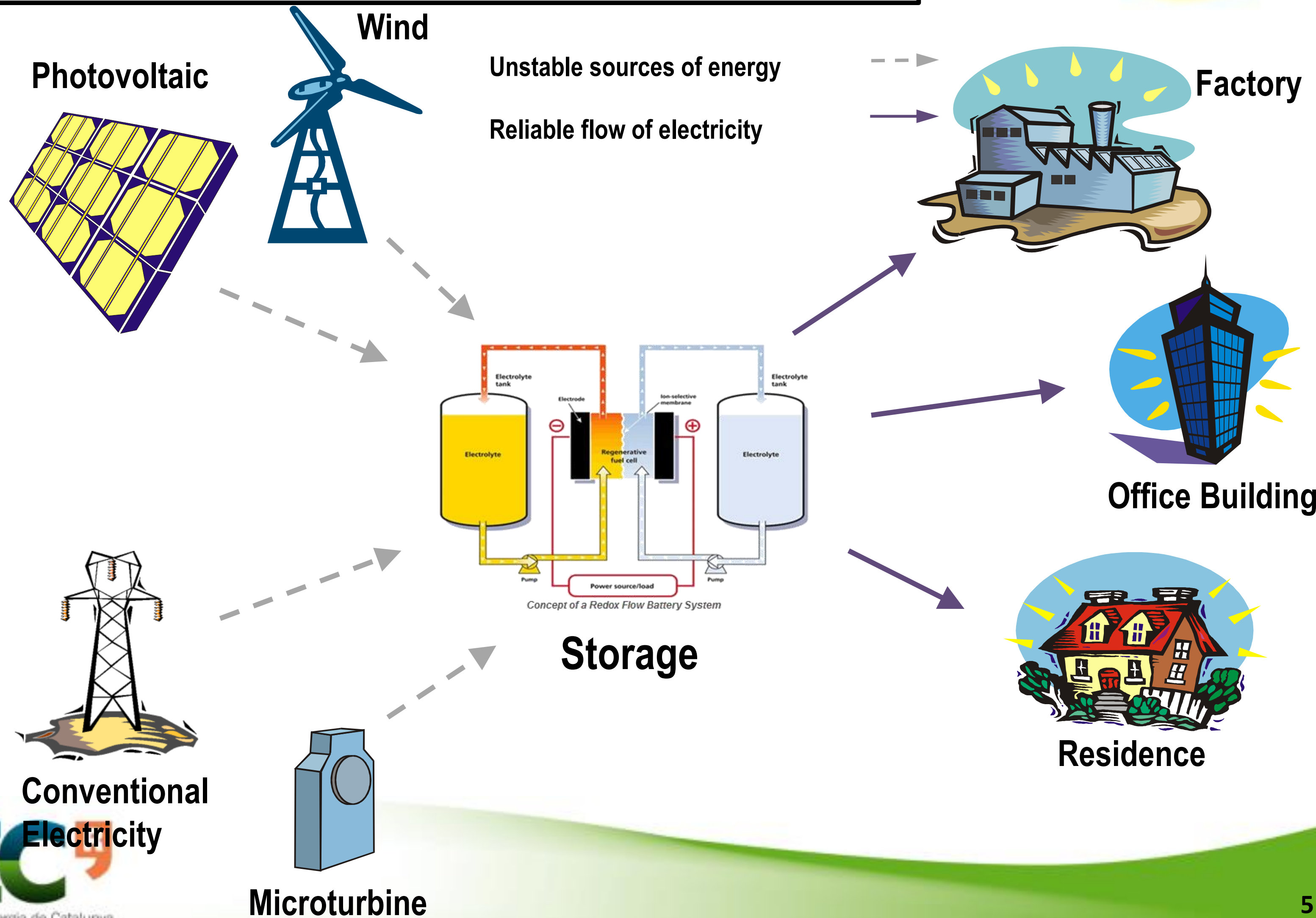
ELECTROCHEMICAL ENERGY STORAGE: VANADIUM REDOX FLOW BATTERIES



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INTRODUCTION: VANADIUM REDOX FLOW BATTERIES

redOx 2015

Cells number: 20
Voltage: 30V
Current: 50 A
Power: 1.5 kW

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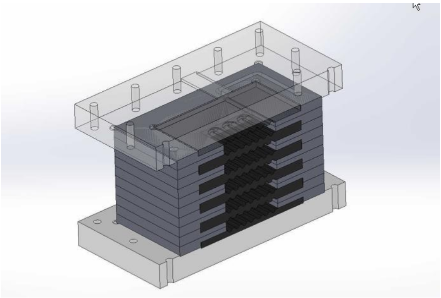

Electrodes

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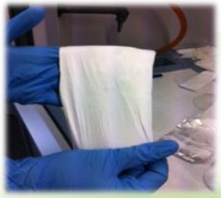
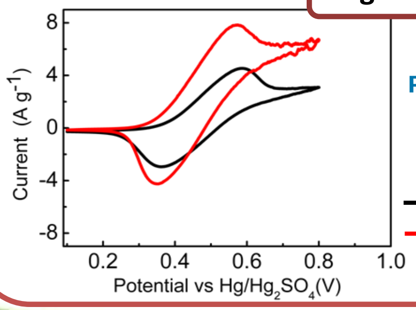
Innovative membranes



High energy density electrolyte



Polymeric additives in aqueous electrolytes

standard electrolyte
0.6% additive-containing electrolyte

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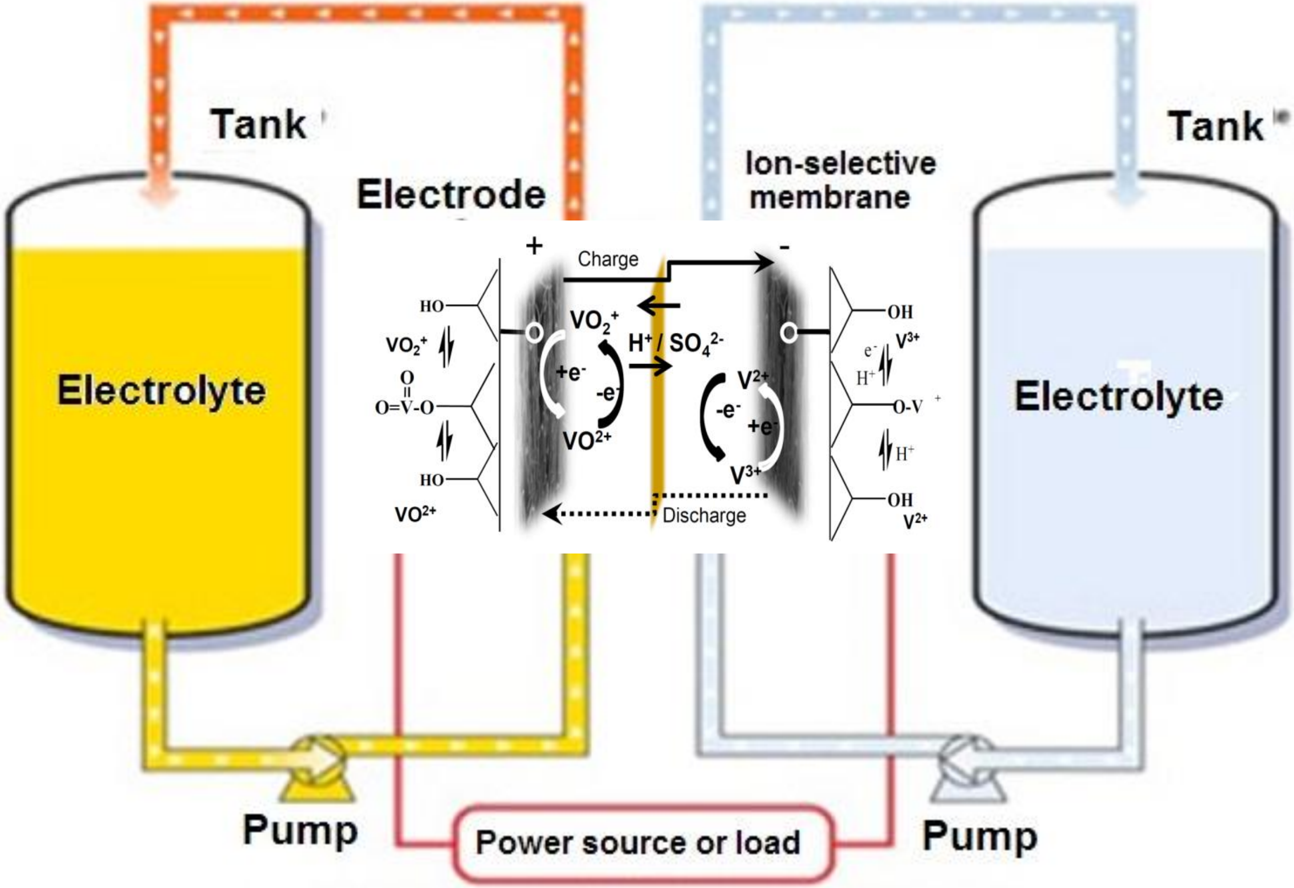
INTRODUCTION: VANADIUM REDOX FLOW BATTERIES

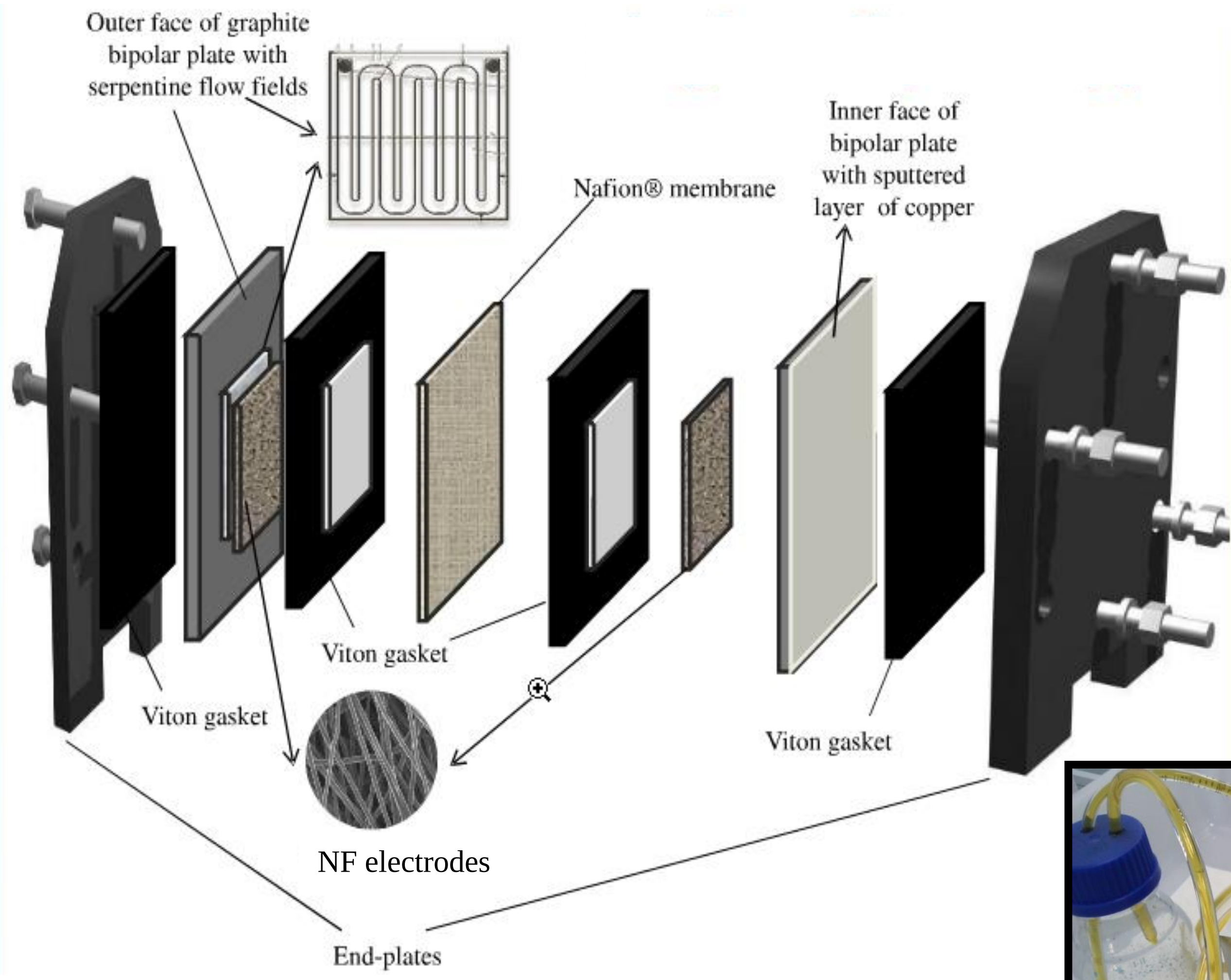
$\mathbf{V^{2+}} \rightarrow \mathbf{V^{3+}} + 1e^-$

$\underline{\mathbf{VO_2^+} + 2H^+ + 1e^- \rightarrow \mathbf{VO^{2+}} + H_2O}$

global: $\mathbf{V^{2+}} + \mathbf{VO_2^+} + 2H^+ \rightarrow \mathbf{V^{3+}} + \mathbf{VO^{2+}} + H_2O$

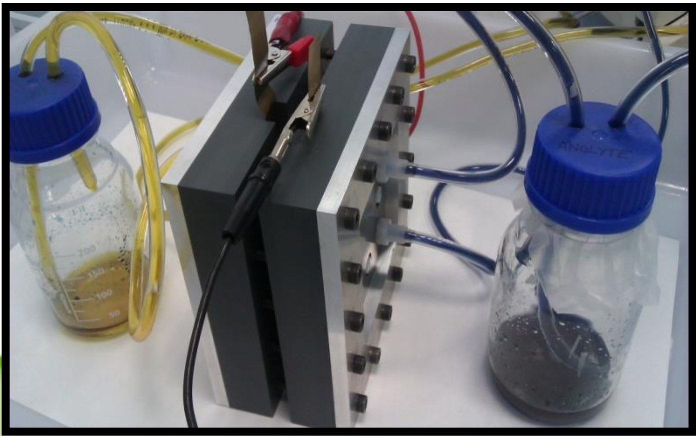


EXPERIMENTAL PART: SINGLE –CELL VRB SYSTEM



Electrodes : 4 cm^2 of geometric area

Electrolyte solution:
20 mL of 1 M Vanadium ion + 3 M H_2SO_4



EXPERIMENTAL PART: ELECTRODE PREPARATION

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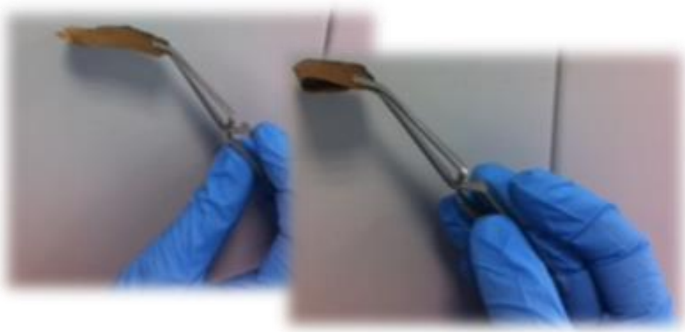
ELECTROSPINNING TECHNIQUES and THERMAL TREATMENTS :

- ✓Synthesis simple, cost-effective and facile
- ✓Large-surface area and binder-free electrodes
- ✓Flexible electrodes for new design of batteries
- ✓Very suitable for large-scale application

Electrospinning nanofiber web



Oxygen –Stabilized web

As-Carbonized NF electrode

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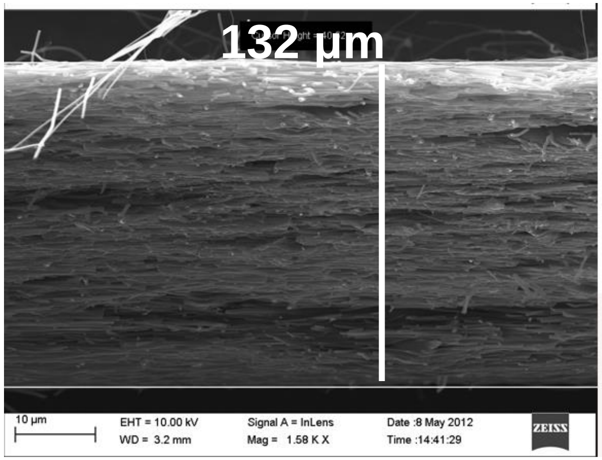
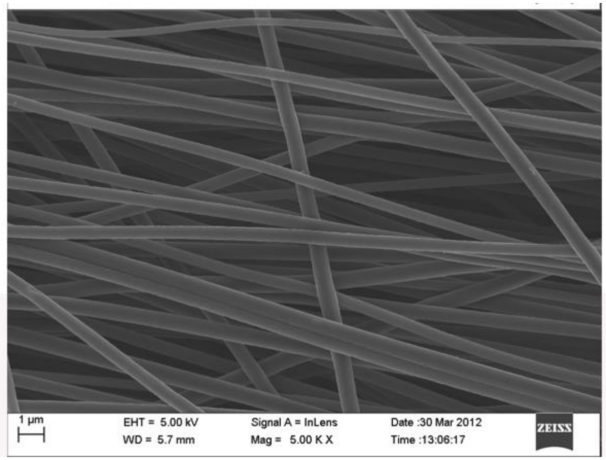
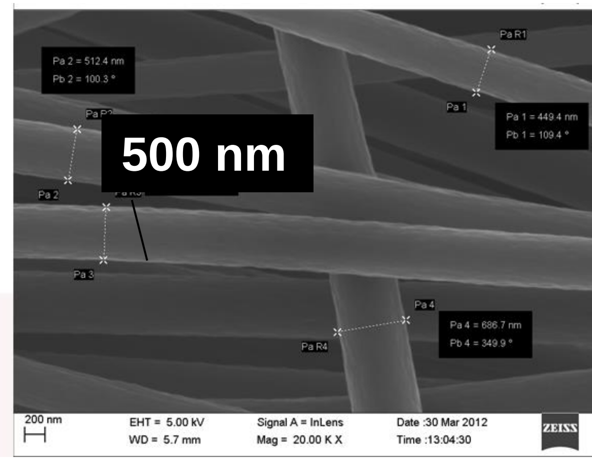
RESULTS: MORPHOLOGICAL CHARACTERIZATION OF NF ELECTRODES

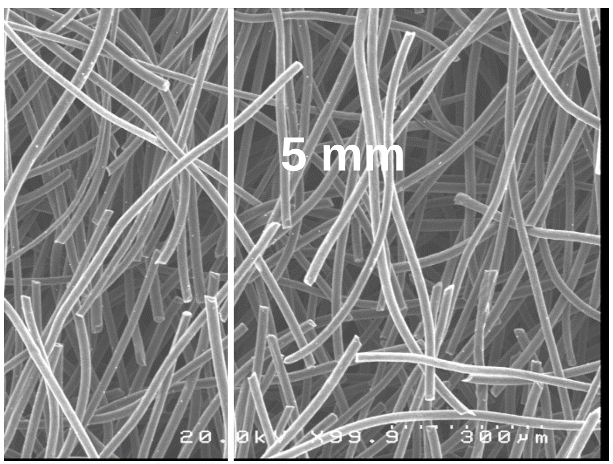
NANOFIBER FE-SEM images

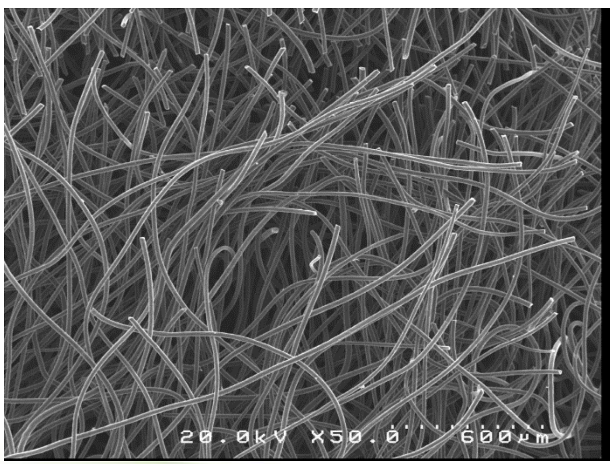


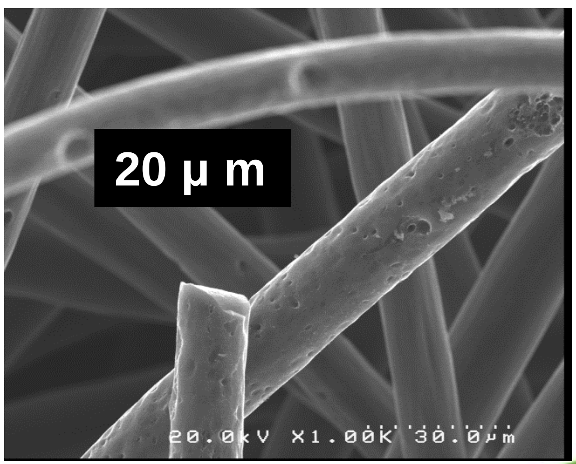




PAN-felt FE-SEM images







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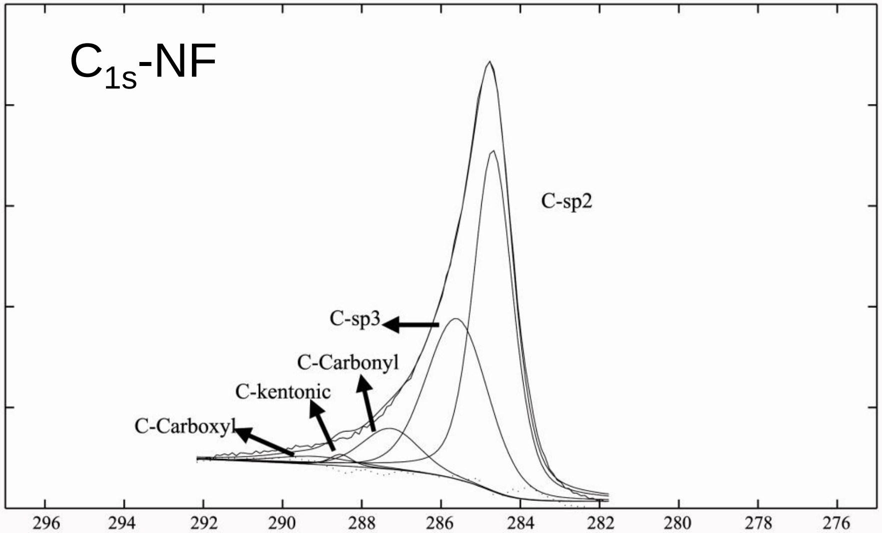
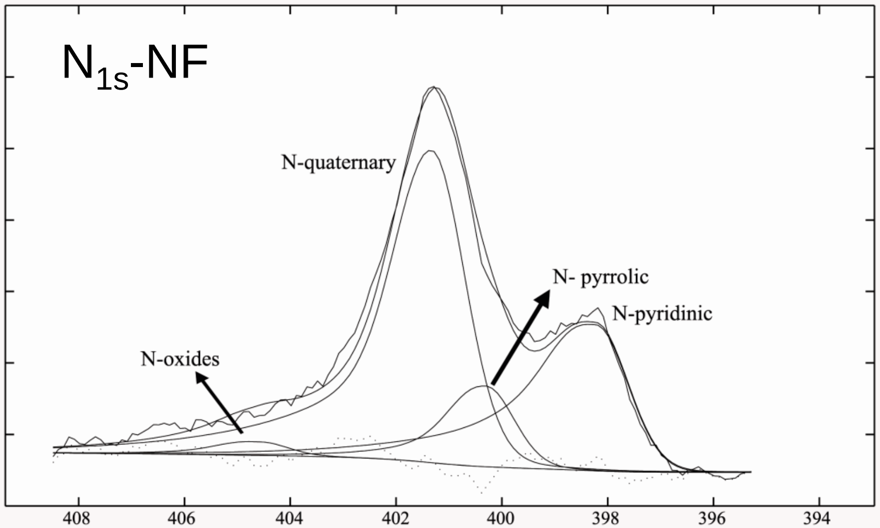
RESULTS : XPS ANALYSIS and ELECTRICAL CONDUCTIVITY

NANOFIBER XPS analysis



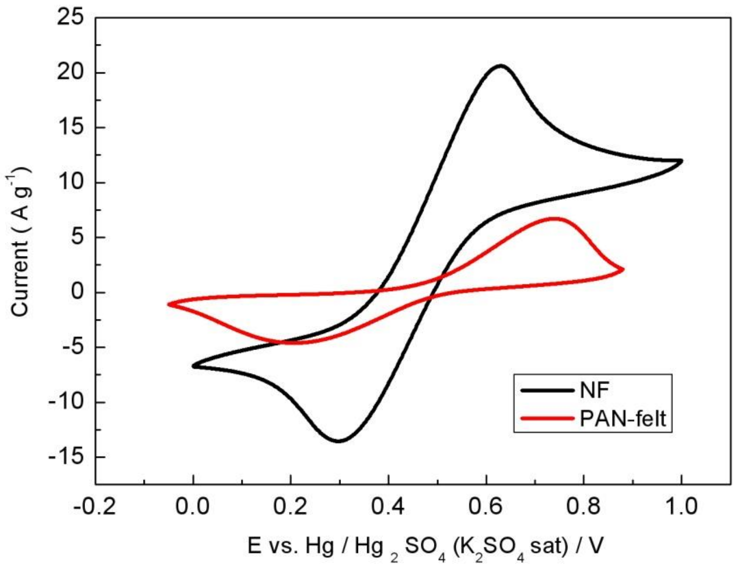


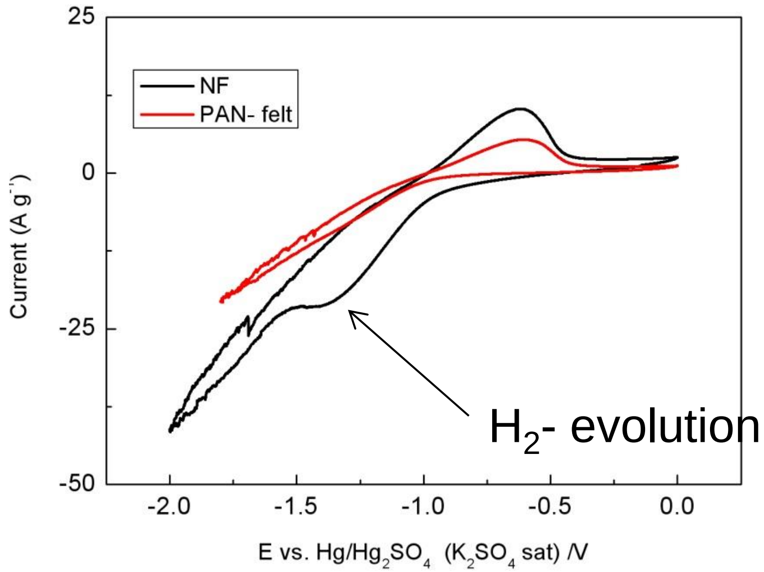
Electrode	Electrical conductivity (S cm^{-1})	Species concentration (atomic %)		
		C	O	N
NF	25.03(16.21)*	88.46	6.61	4.93
PAN-felt	3.65	77.00	22.30	0.70

* Electrical conductivity parallel to the winding direction, in parenthesis perpendicular to the winding direction

$\mathbf{VO_2^+} + 2H^+ + 1e^- \rightarrow \mathbf{VO^{2+}} + H_2O$

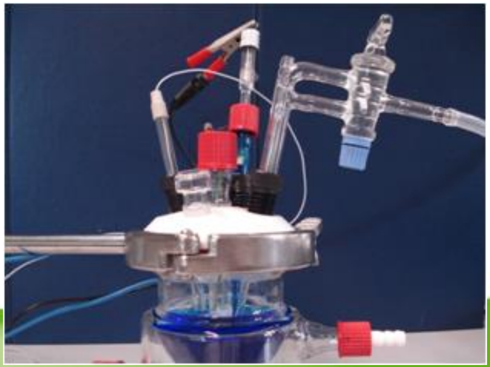
$\mathbf{V^{2+}} \rightarrow \mathbf{V^{3+}} + 1e^-$





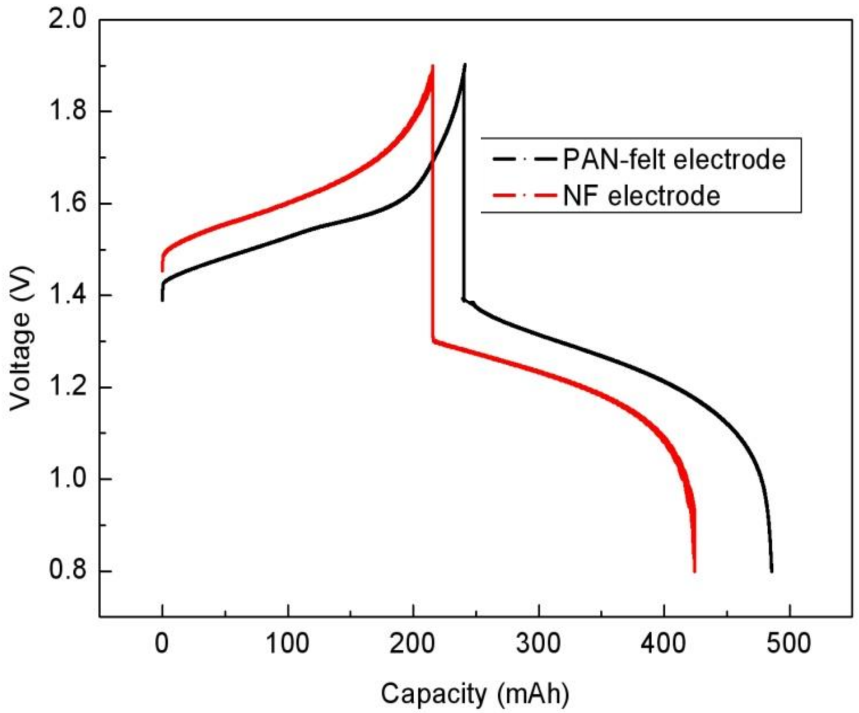
30 cm^3 of a 0.5 mol dm^3 Vanadium ion in 3 mol dm^3 H_2SO_4 solution. Scan rate: 5 mV s^{-1}

Negative reaction suffer kinetic limitation



[1] G. Oriji, Y. Katayama, T. Miura, Electrochim. Acta 49 (2004) 3091

➢COMPARATION WITH COMMERCIAL ELECTRODES



Current density: 25 mA cm^{-2}

Flow rate : 12 mL min^{-1}

Electrode	EE	Discharge energy (WhL^{-1})	Discharge capacity (mA h)
NF	76.94	14.13	226.78
PAN-felt	77.74	16.28	243.56

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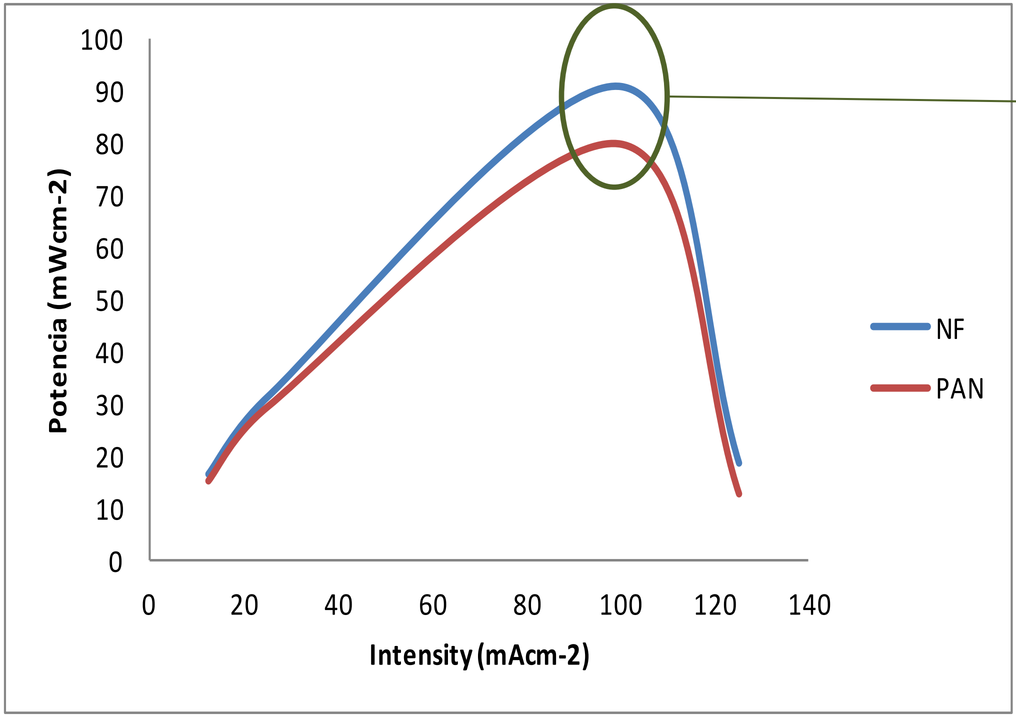
➢ COMPARATION WITH COMMERCIAL ELECTRODES



NF: Pmax = 91 $mWcm^{-2}$

PAN-felt: Pmax= 80 $mWcm^{-2}$

Weight NF: 0.013 g

Weight PAN-felt: 0.229 g

Decrease of stack size

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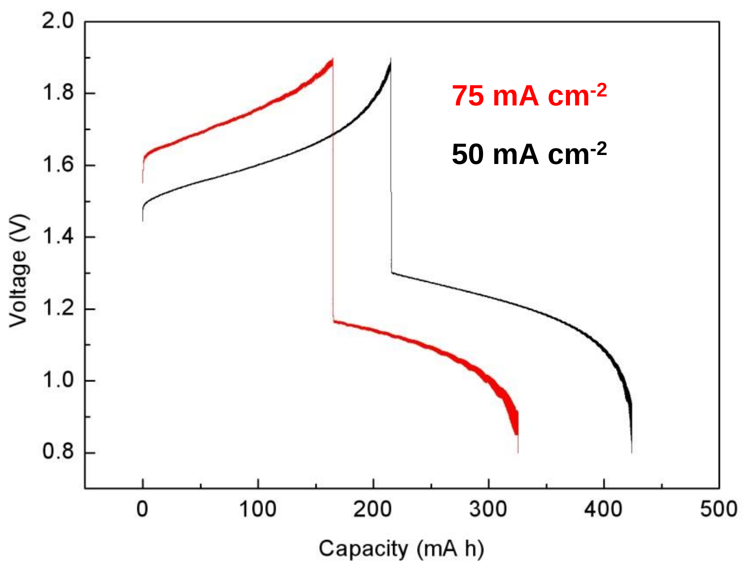
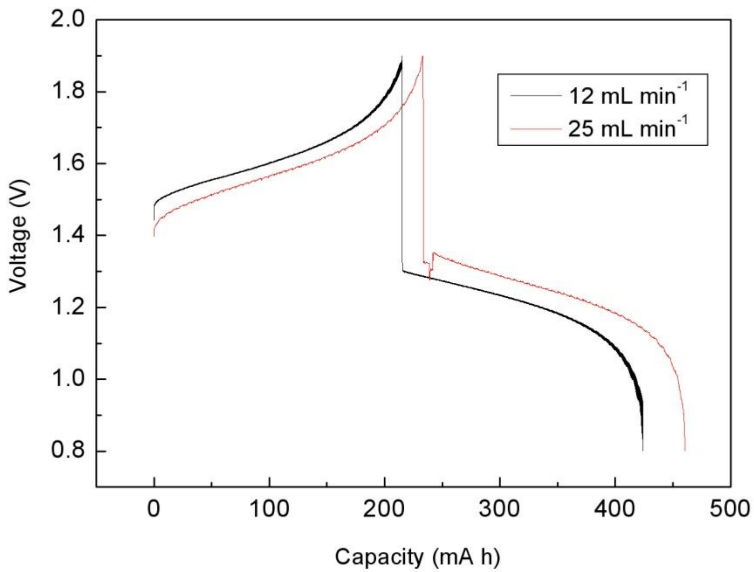
RESULT: NF electrode assembled in VRFB PROTOTYPE

➢CURRENT DENSITY AND FLOW RATE DEPENDENCE





Current density ($mA\ cm^{-2}$)	Flow rate ($mL\ min^{-1}$)	CE	VE	EE
25 $mA\ cm^{-2}$	12$mLmin^{-1}$	96.94	75.69	73.38
50 $mA\ cm^{-2}$	12$mLmin^{-1}$	97.74	63.51	62.08
75 $mA\ cm^{-2}$	12$mLmin^{-1}$	99.10	50.74	50.28
25 $mA\ cm^{-2}$	25 $mLmin^{-1}$	97.29	78.79	76.66

BEST CONDITIONS

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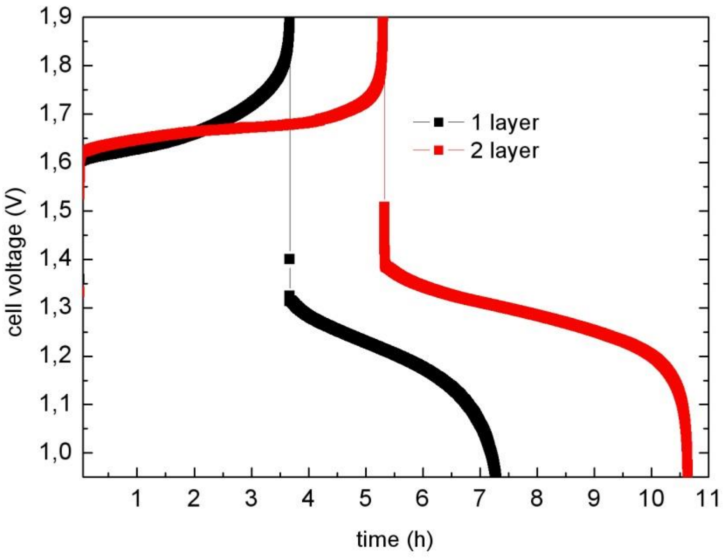
➢ELECTROCATALYTIC EFFECT OF NANOFIBER



Theoretial capacity: 539 mAh

Electrode	Capacity /mAh
1 LAYER NF	220
2 layer NF	412.5

Experimental condition:

75 mA cm^{-2}

25 $mLmin^{-1}$

EE up to 84%

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CONCLUSIONS

- Highly electrocatalytic nanofiber such as electrode material for VRB has been test for the first time showing similar efficiencies that commercial PAN-felt electrode.
- Slightly increment of the power maximum of the VRB have been demonstrated.
- Increment of the capacity of the system with layer of the nanofiber demonstrating the catalytic affect of NF electrode.

Cristina Flox, Cristian Fàbrega, Teresa Andreu, Alex Morata, Marcel Skoumal, Javier Rubio-Garcia and Juan Ramón Morante . Highly electrocatalytic flexible nanofiber for improved vanadium-based redox flow battery cathode electrodes.
RSC Adv., 2013,3, 12056-12059

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THANK YOU FOR YOUR ATTENTION !

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