


The CEA logo consists of the lowercase letters 'cea' in a white, rounded, sans-serif font, positioned on a red square background. A thin green horizontal line is located below the letters.

cea

An aerial photograph of a large research facility, likely CEA-LITEN, featuring several large industrial-style buildings with solar panels on the roofs, surrounded by green fields and a road. In the background, there are mountains and a lake under a blue sky with scattered clouds.

Cyclic ageing of titanium-supported lead dioxide electrodes for bipolar battery applications

A. Kirchev, L. Serra , B. Marie

Université Grenoble Alpes, CEA-LITEN, DTS, INES, Grenoble, F-38000, France

The ELBC logo features a stylized blue icon of a flower or a cluster of dots on the left, followed by the text 'ELBC' in a bold, blue, sans-serif font.

**ELBC**  
6-9 September  
Lyon, France 2022

The INES logo features a stylized orange sun icon on the left, followed by the text 'ines' in a bold, black, sans-serif font, and 'INSTITUT NATIONAL DE L'ENERGIE SOLAIRE' in a smaller, black, sans-serif font below it.

**ines**  
INSTITUT NATIONAL  
DE L'ENERGIE SOLAIRE

# TITANIUM FOIL AS A KEY COMPONENT OF THE BIPOLAR LEAD-ACID BATTERY

## Readily available advantages:

- Highly abundant and non-toxic chemical element
- Exceptional corrosion resistance at the potentials above 0 V vs. SHE
- High tensile strength allowing the use of thin foils (< 50  $\mu\text{m}$ )
  - Minimum use of titanium in a laminated Pb-Ti bilayer current collector
  - Potential weight and volume gains



## The Surface treatment is mandatory:

- Deposition of F- and/or Sb- doped  $\text{SnO}_2$  conductive films preventing the surface from passivation (formation/growth of resistive  $\text{TiO}_2$  layers)
- Ti- $\text{SnO}_2$  surface offers good compatibility with the positive active material \*



## Key issues:

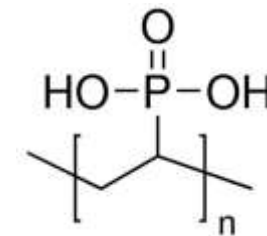
- Rather poor positive active material cyclic capacity retention \*

\* J. Lannelongue et al., "Operation of thin-plate positive lead-acid battery electrodes employing titanium current collectors", *J Energy Storage* 20 (2018) 230

# PHOSPHATE DOPING OF THE POSITIVE PLATE AS POTENTIAL CAPACITY RETENTION STRATEGY

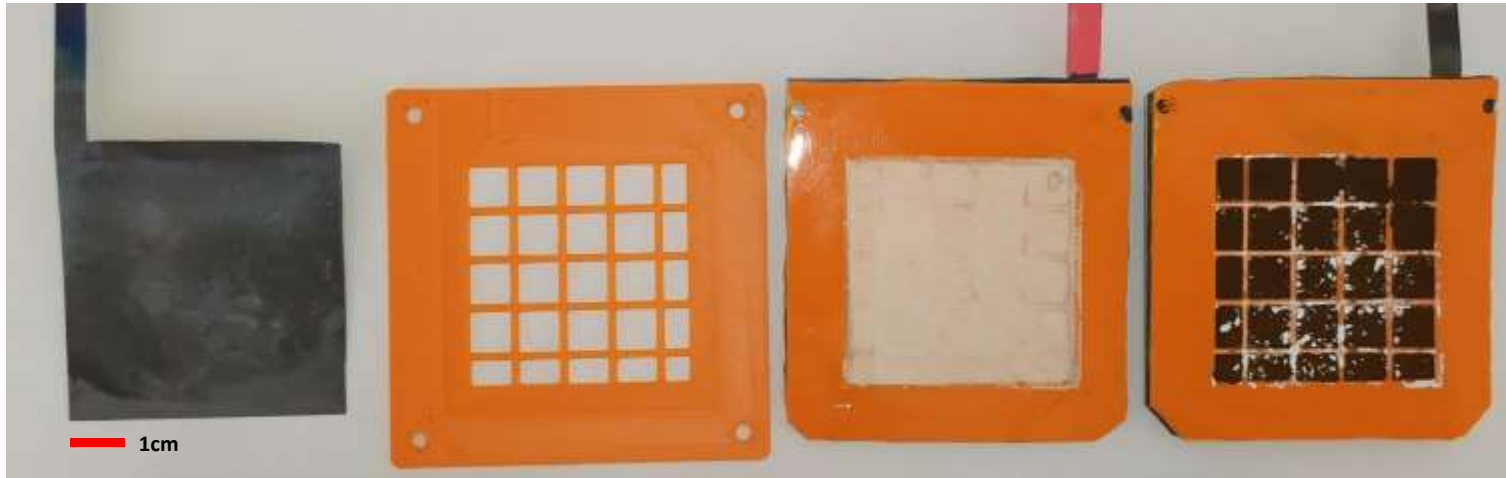
$\text{H}_3\text{PO}_4$  added in the electrolyte after the formation leads to slightly lower PAM utilization and improved capacity retention (*E. Voss, J Power Sources 24 (1988) 171*)

- $\text{H}_3\text{PO}_4$  in the electrolyte for jar formation
  - ✓ Inhibiting effect in 5M  $\text{H}_2\text{SO}_4$  with  $[\text{H}_3\text{PO}_4] > 1\%$  (*G.A. Morris, PhD thesis, December 1992*)
  - ✓ Promoting effect at 2.5M  $\text{H}_2\text{SO}_4 + 1\% \text{H}_3\text{PO}_4$  (*A. Lannelongue et al., EP 3474352 (A1) — 2019-04-24*)
- $\text{CaHPO}_4$  in the positive paste
  - Slow local doping effect throughout the reaction
    - $\text{CaHPO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_3\text{PO}_4$
- Poly-vinylphosphonic acid (PVPA) in the positive paste
  - Polymer binder effect (expected mitigation of the PAM softening)
  - Long-chain molecules with reduced mobility (local effects)
  - Possible adsorption on the  $\text{PbO}_2$  surface  $\rightarrow$  particle size control



**PVPA**

## EXPERIMENTAL SET-UP: ELECTRODES AND CELLS



Ti-SnO<sub>2</sub> current collector

3D printed PAM supporting grid

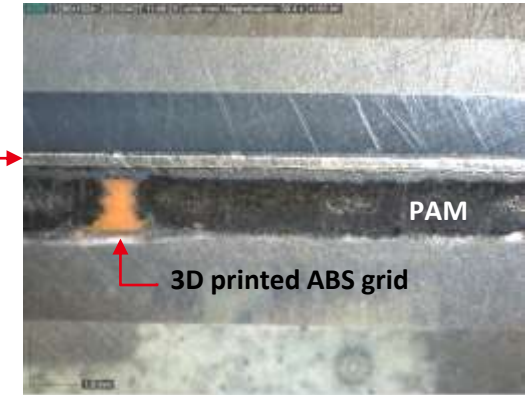
Cured electrode

Formed electrode

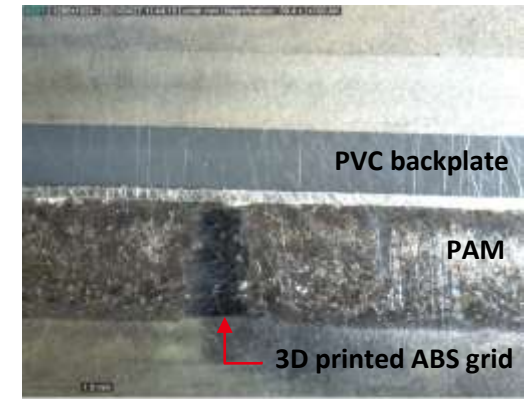
- ✓ 3D printed paste supporting plastic grid (Grosvenor and Pinsky, US 5 800 946)
- ✓ AGM separators, 220 g/m<sup>2</sup> (Bernard Dumas, France), 2 layers and 3 layers / 2.5M H<sub>2</sub>SO<sub>4</sub> electrolyte: (1.15 s.g.; pure or containing 1% H<sub>3</sub>PO<sub>4</sub>); DYNAGRID® NG pasting paper
- ✓ Ag/Ag<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> reference electrodes
- ✓ Oversized conventional negative electrodes
- ✓ Four paste batches (PAM doped with CaHPO<sub>4</sub>, Poly-vinylphosphonic acid and/or fumed silica)
- ✓ 72h – long jar formation process

Ti foil  
0,25mm

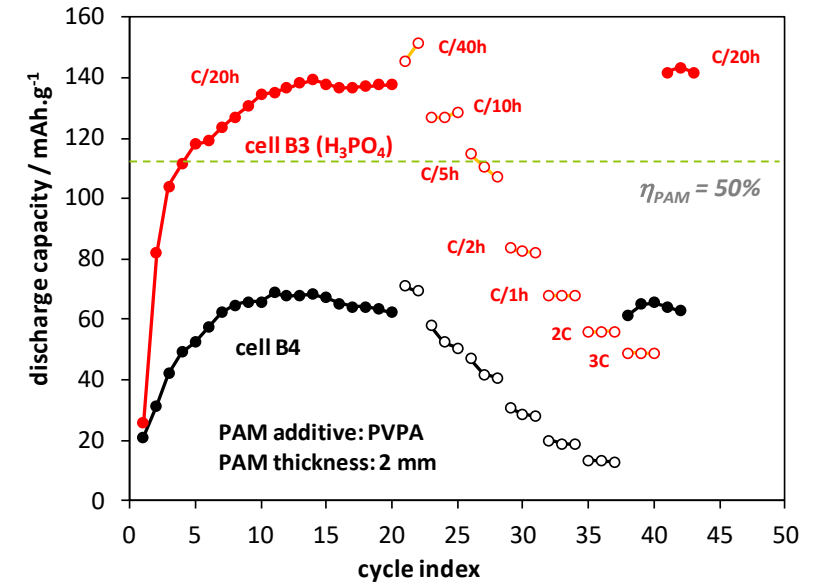
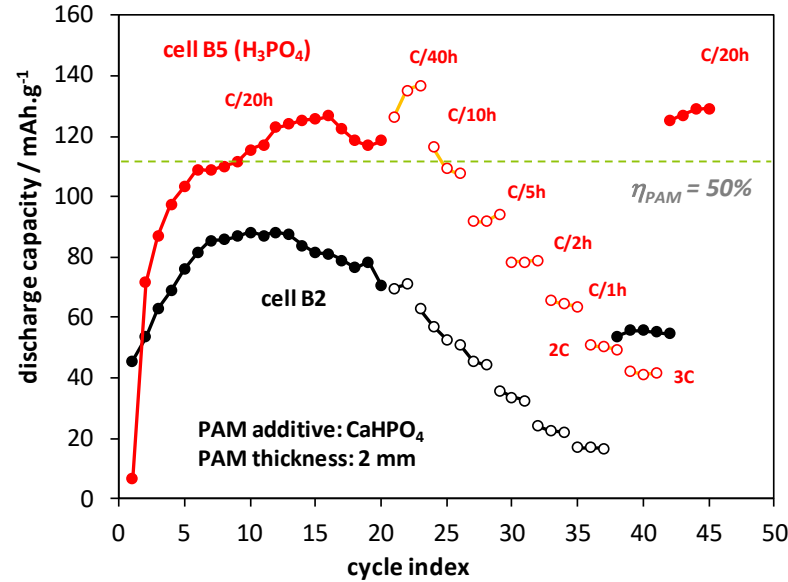
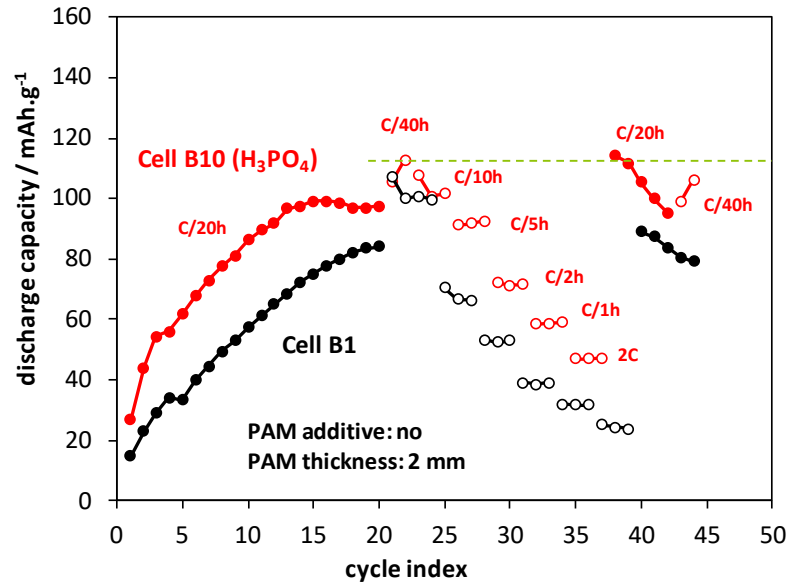
Electrode with 1 mm thick PAM  
2 layer AGM compressed to 1,8 mm



Electrode with 2 mm thick PAM  
3 layer AGM compressed to 2,7 mm

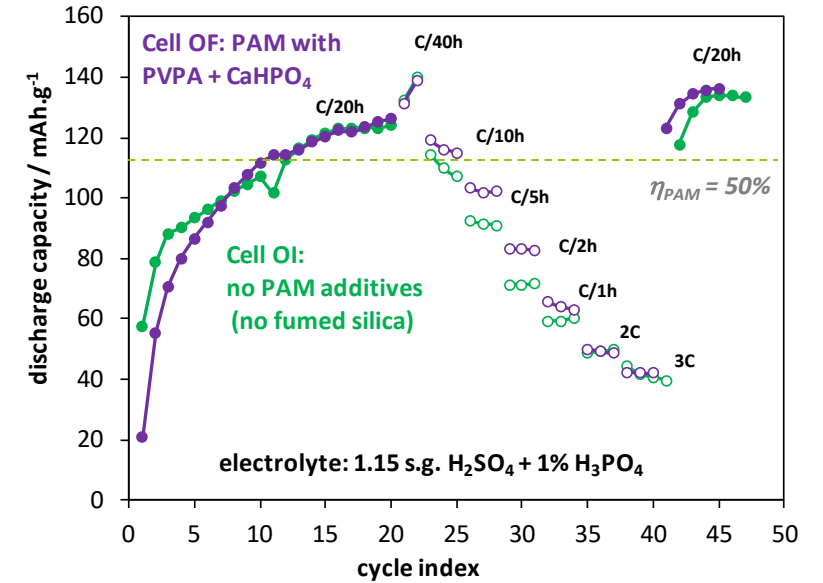
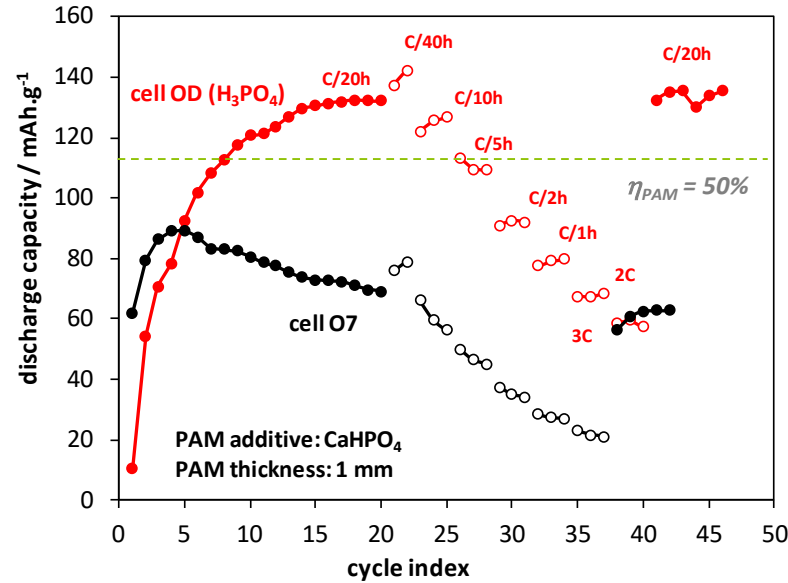
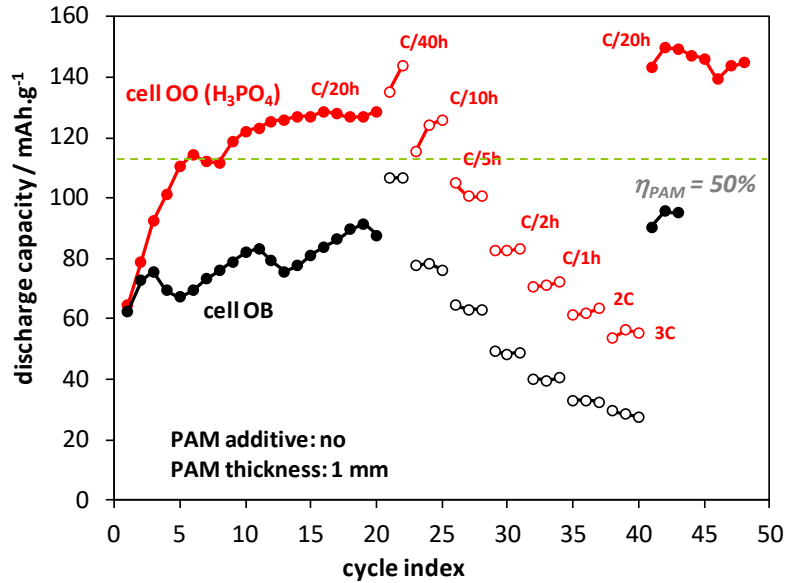


# INITIAL PERFORMANCE OF THICK ELECTRODES



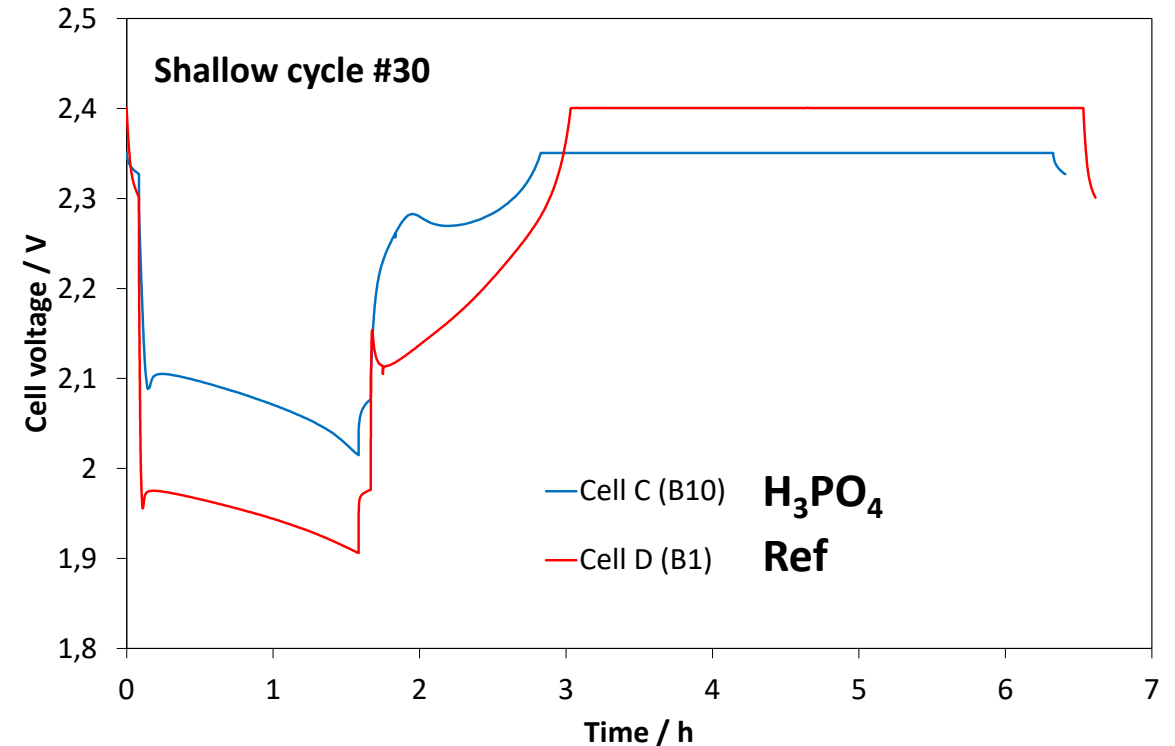
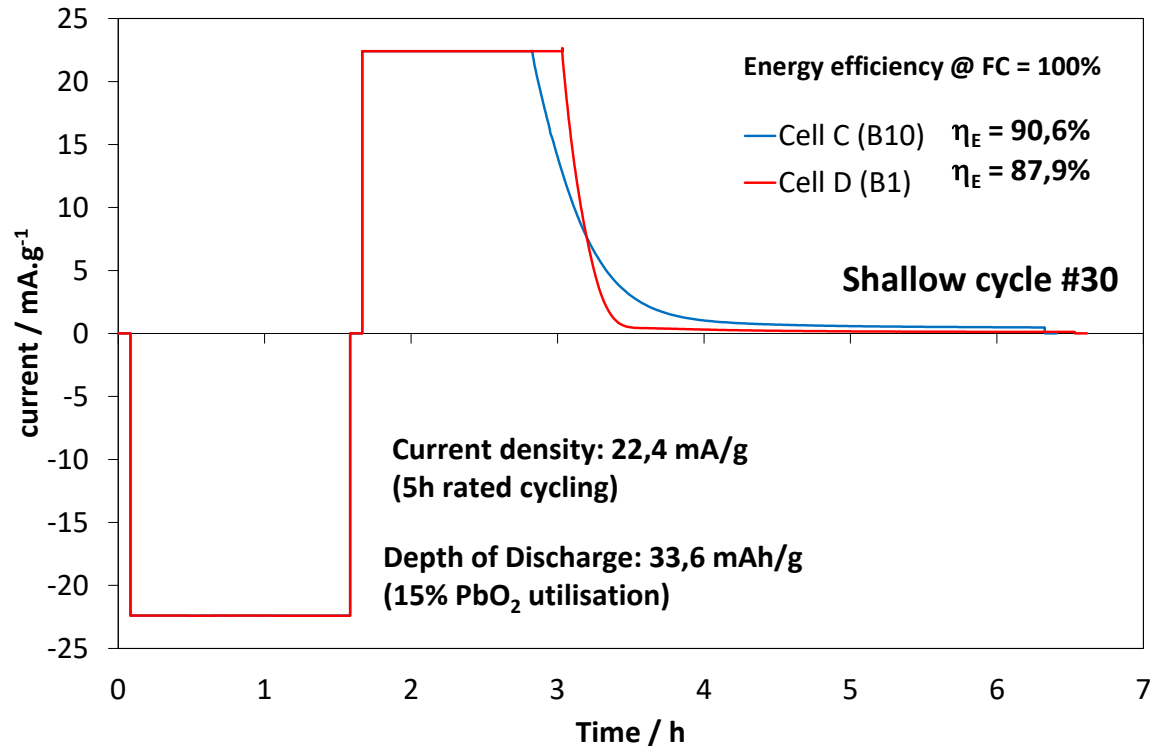
- ✓ The jar formation in the presence of H<sub>3</sub>PO<sub>4</sub> results in improved positive active material (PAM) utilization in a wide range of discharge rates (from C/20h to 3C)
- ✓ The use of PAM additives containing different types of phosphate derivatives causes a synergy effect with the addition of H<sub>3</sub>PO<sub>4</sub> to the jar-formation electrolyte
- ✓ Good initial capacity retention

# INITIAL PERFORMANCE OF THINNER ELECTRODES



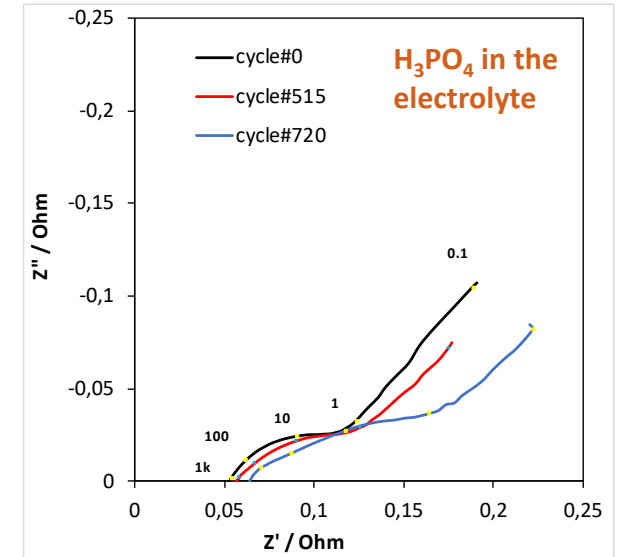
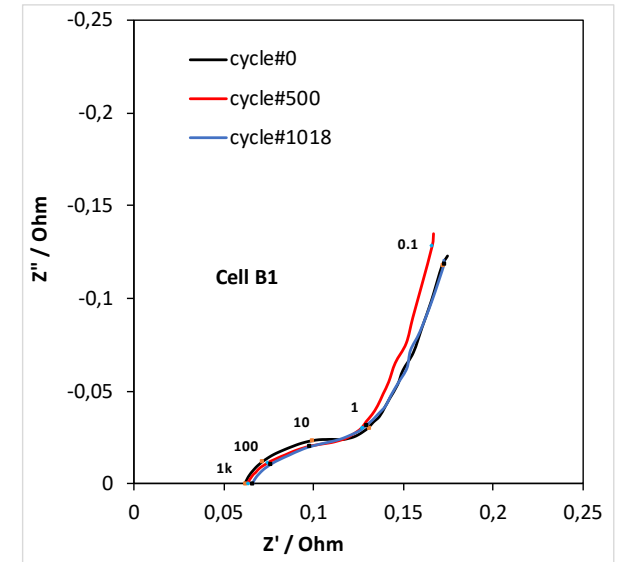
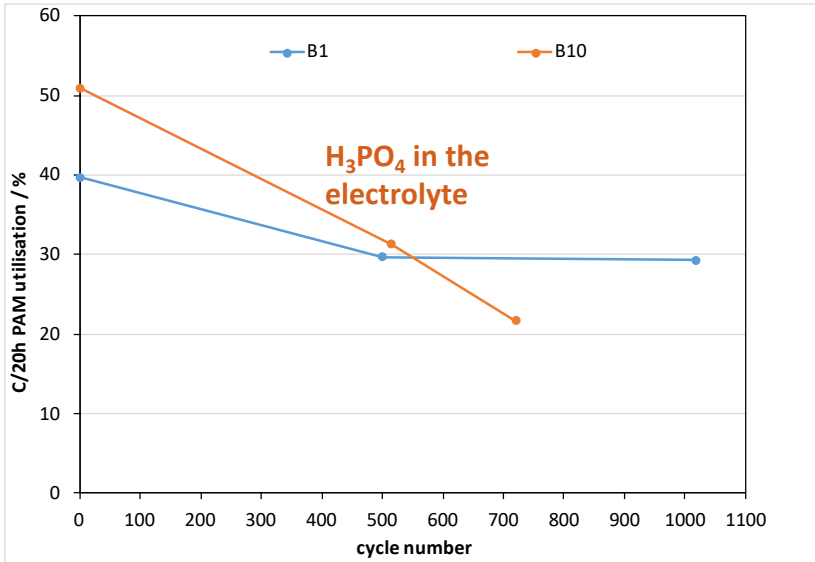
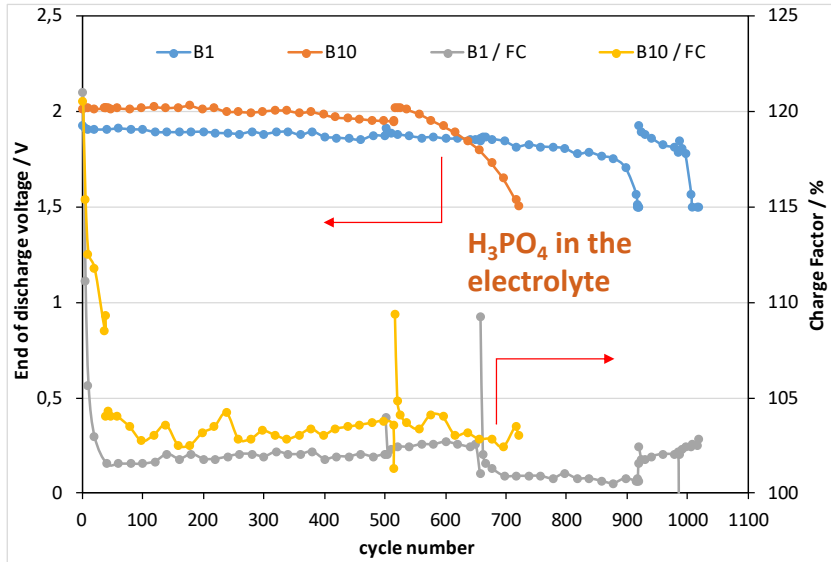
- ✓ The decrease of the electrode thickness to 1mm leads to further improvement of the discharge performance of the electrodes formed in the presence of H<sub>3</sub>PO<sub>4</sub>
- ✓ The synergy effect between the PAM additives and the H<sub>3</sub>PO<sub>4</sub> from the electrolyte is less obvious
- ✓ The results indicate that the effect of the electrolyte diffusion is critical

## CYCLE AGEING TEST SCHEDULE



- Cycling with a limited active material utilization and 5h-rated current (22.4 mA/g @ 1.5h)
- Constant current / Constant voltage charge (voltage limit range: 2,35 – 2,40 V)
- The charge voltage and duration limits are adjusted in order to cycle the cells with charge factor varying in the range of 101 – 105%
- Periodic “check-up” cycles with 20h-rated discharge current followed by impedance measurements at SOC = 100%
- The 20h-rated PAM utilization is used as a parameter accounting the electrochemical activity of the PbO<sub>2</sub> electrode

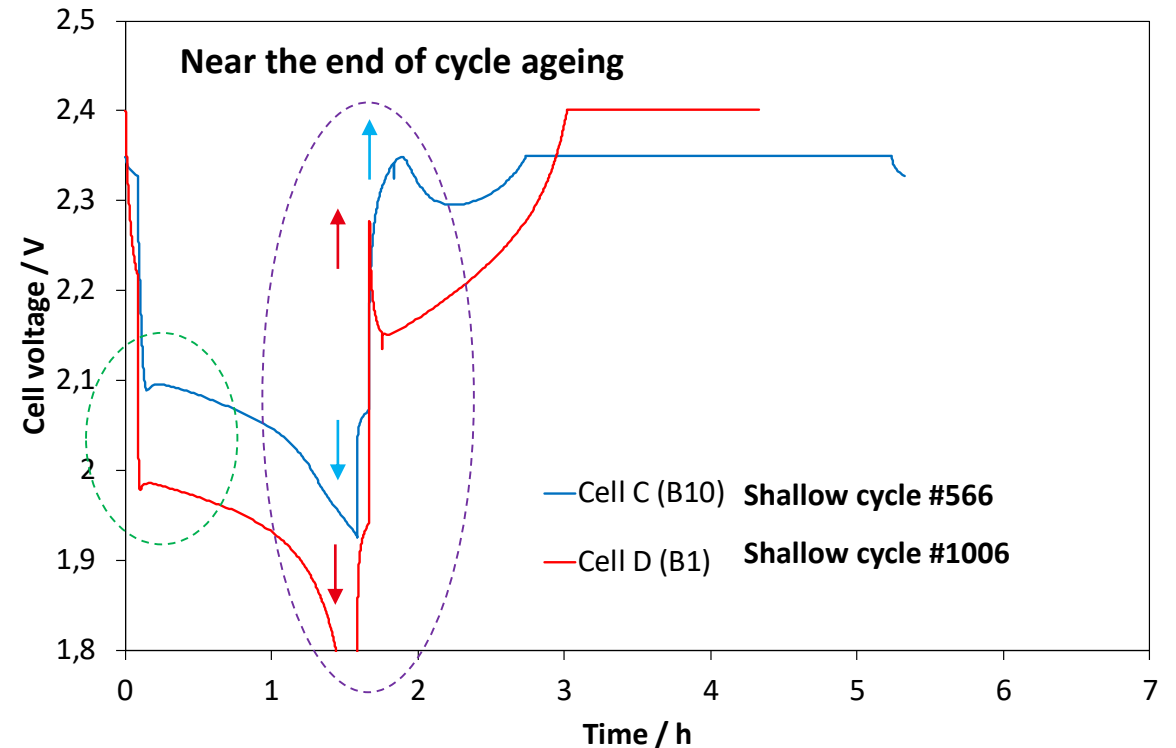
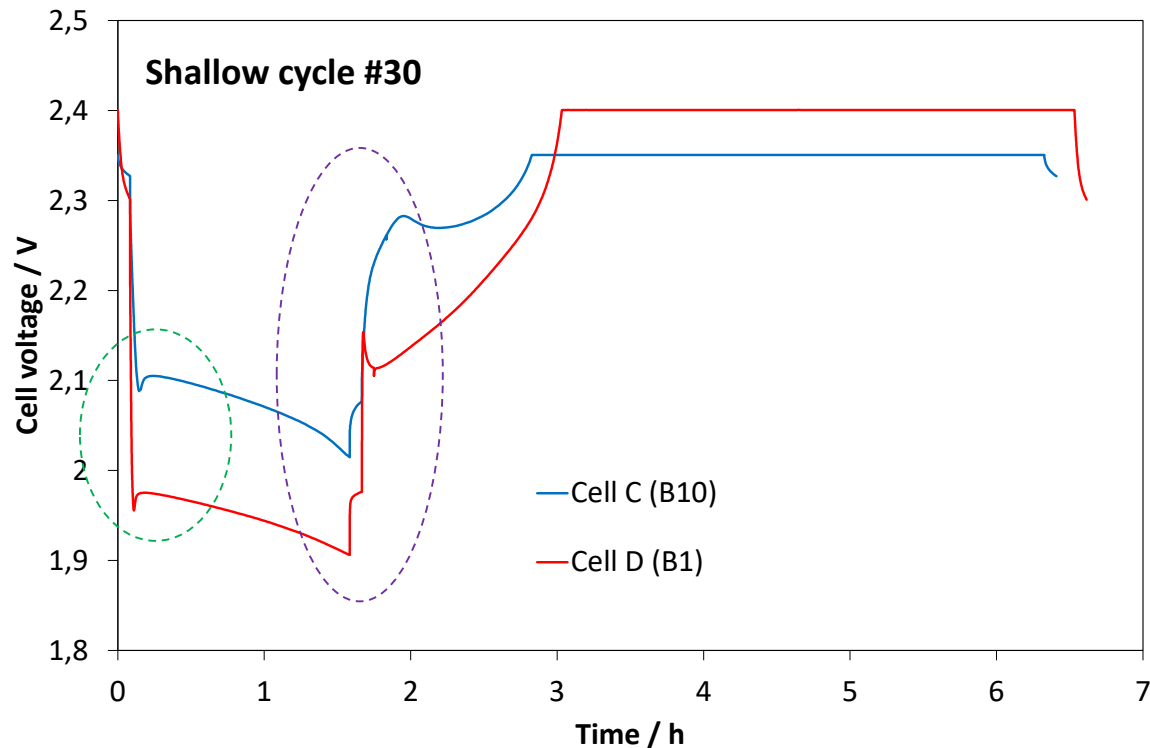
# CYCLE AGEING OF THICK ELECTRODES WITHOUT PHOSPHATES ADDED TO PAM



- The electrode formed with H<sub>3</sub>PO<sub>4</sub> doped electrolyte undergoes an ageing with progressive loss of PbO<sub>2</sub> activity and rather small increase of the ohmic component of the impedance
- The ageing of the non-doped electrode proceeds without any significant increase of the impedance indicating that the performance of the SnO<sub>2</sub>-Ti current collector remains stable



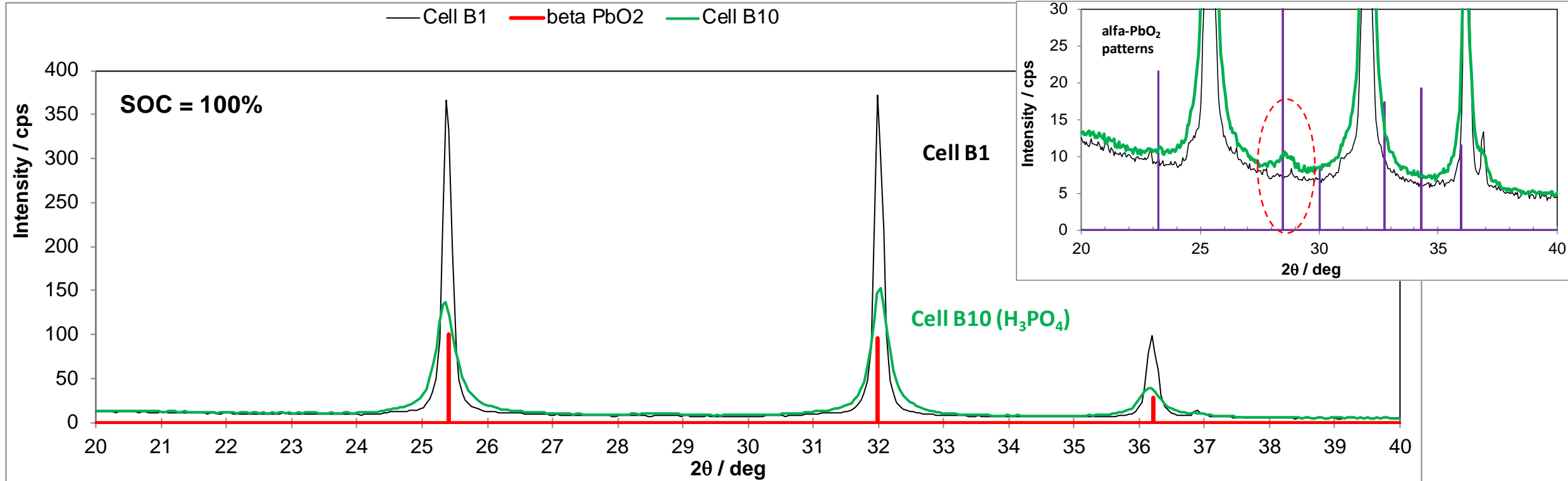
## CYCLE AGEING OF THICK ELECTRODES WITHOUT PHOSPHATES ADDED TO PAM



- The initial discharge stage of the voltage transients are consistent with the impedance measurements and the hypothesis that the current collector ageing is rather slow process
- The cell voltage and the positive electrode transients in the end of the discharge and the beginning of the charge process indicate that the cycle ageing proceeds with the formation of resistive  $PbO_n$  throughout solid-state discharge of the  $PbO_2$  similar to those observed at Sb-free positive plates\*

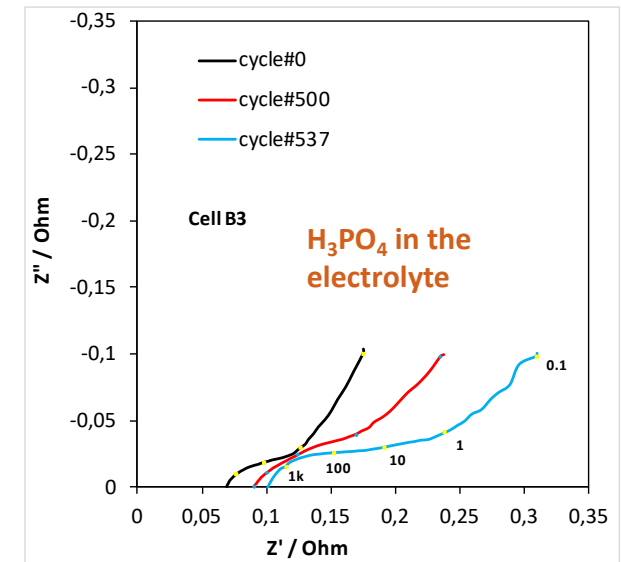
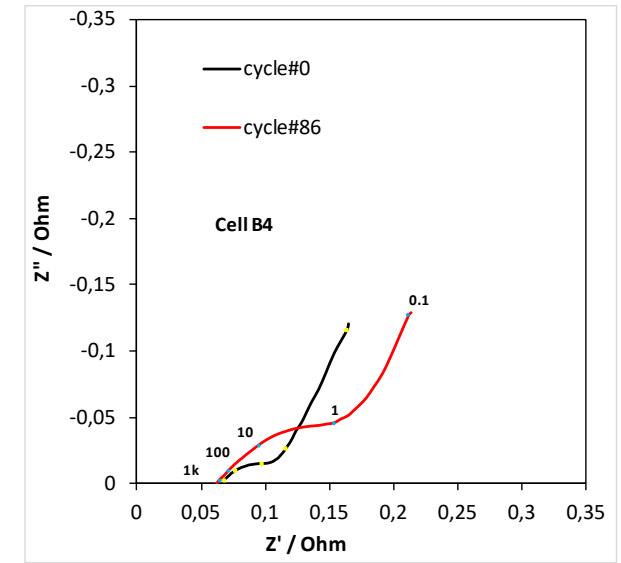
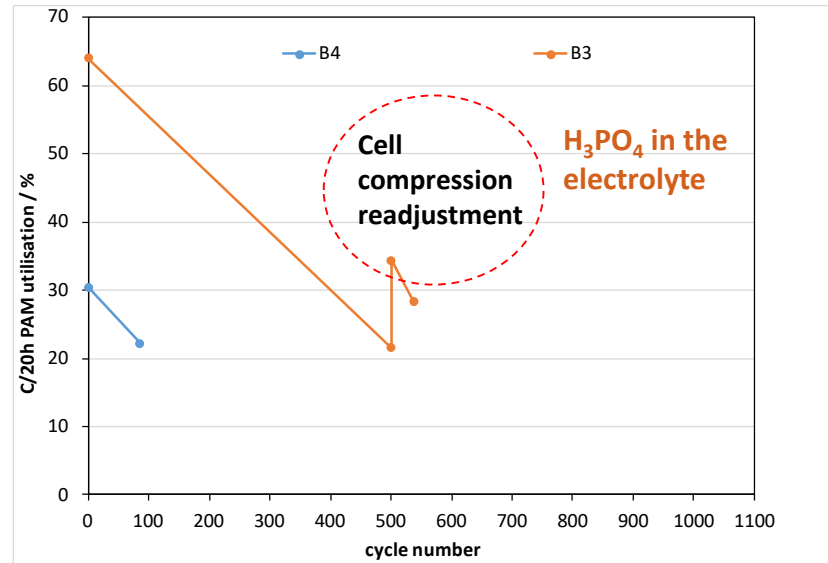
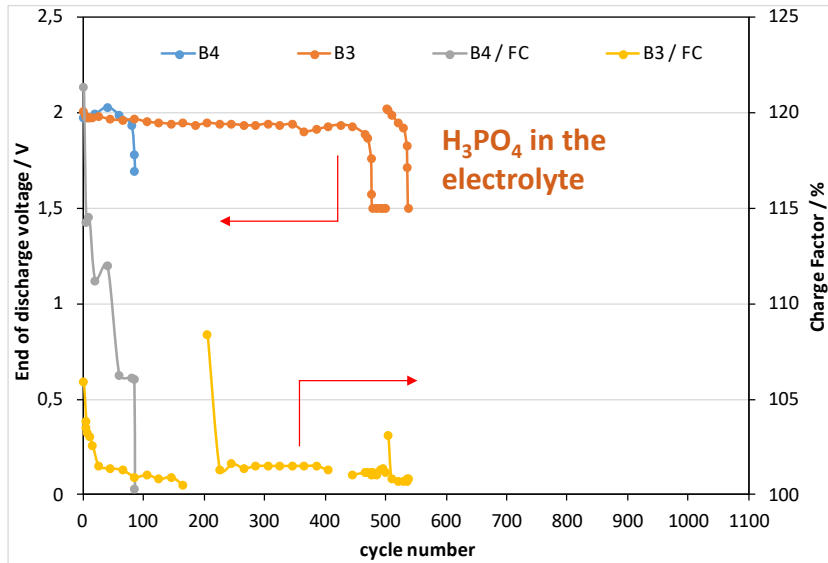
\* D. Pavlov and G. Petkova 2002 J. Electrochem. Soc. 149 A644

## CYCLE AGEING OF THICK ELECTRODES WITHOUT PHOSPHATES ADDED TO PAM



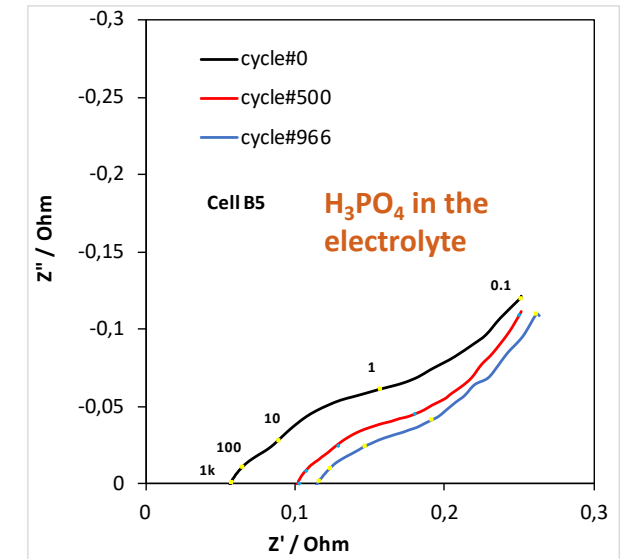
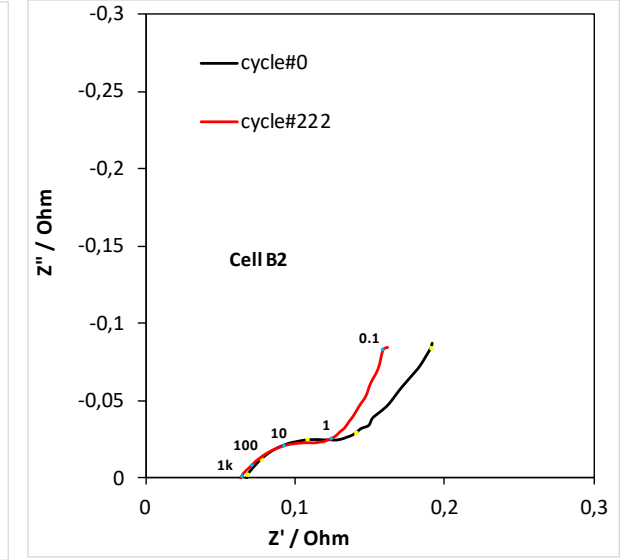
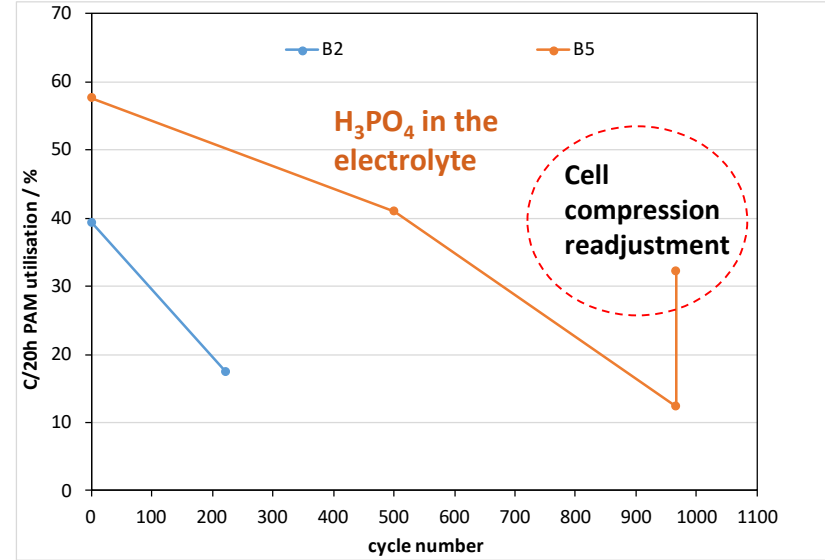
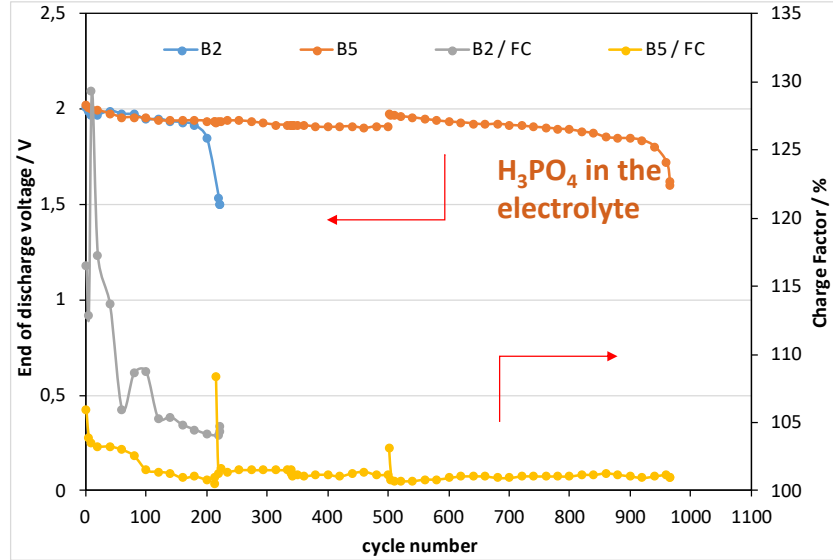
- The crystallographic composition of the aged active materials in completely charged state consists almost entirely of  $\beta$ -PbO<sub>2</sub>
- The addition of H<sub>3</sub>PO<sub>4</sub> decreases markedly the PAM crystals size and promotes the presence of trace amounts of  $\alpha$ -PbO<sub>2</sub>

# CYCLE AGEING OF THICK ELECTRODES WITH PVPA ADDED TO PAM



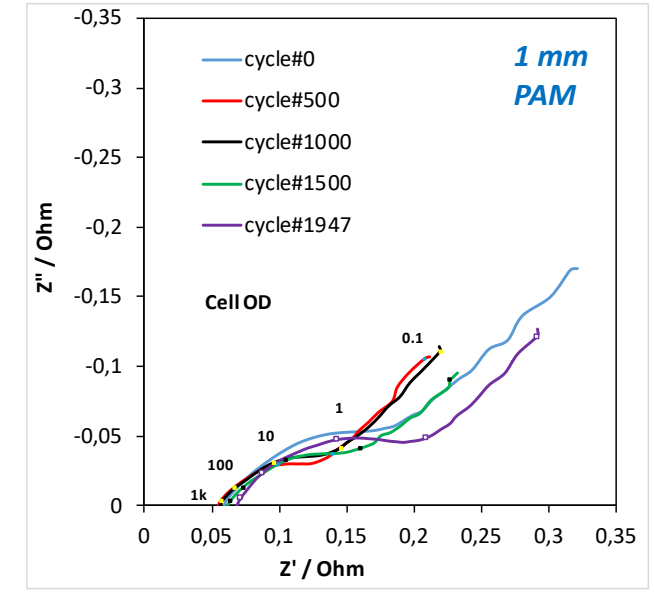
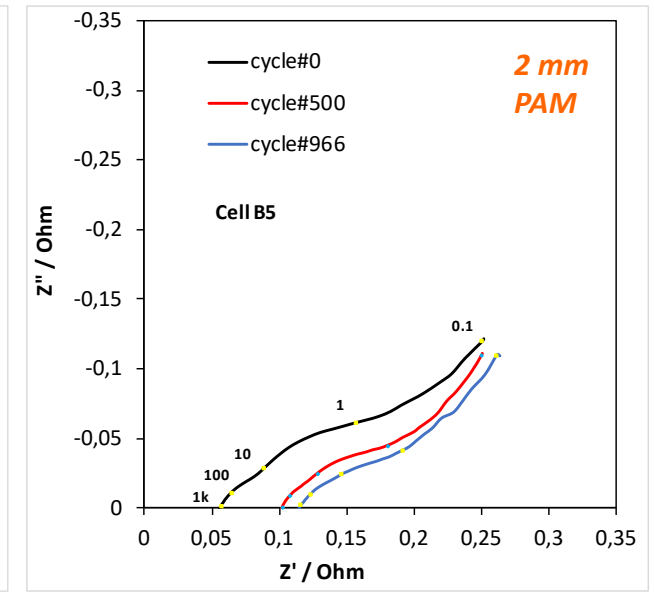
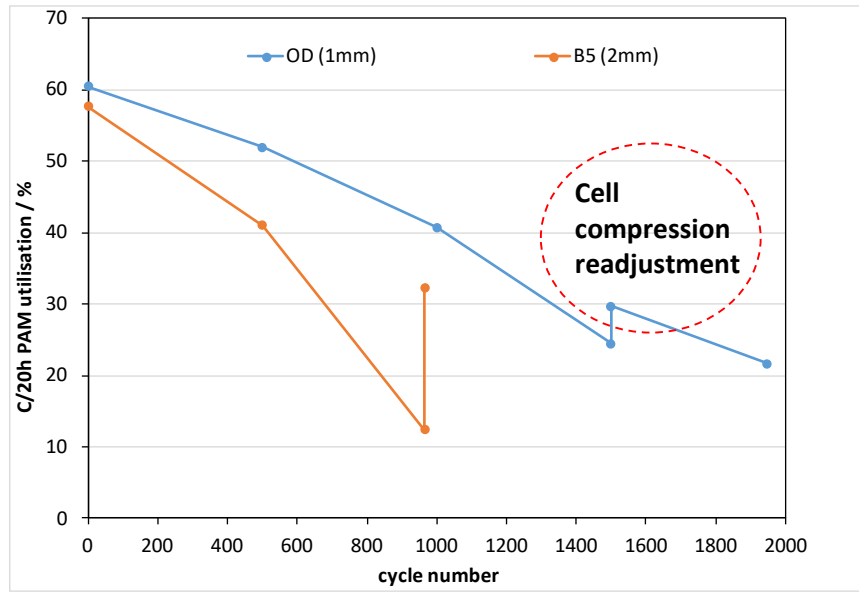
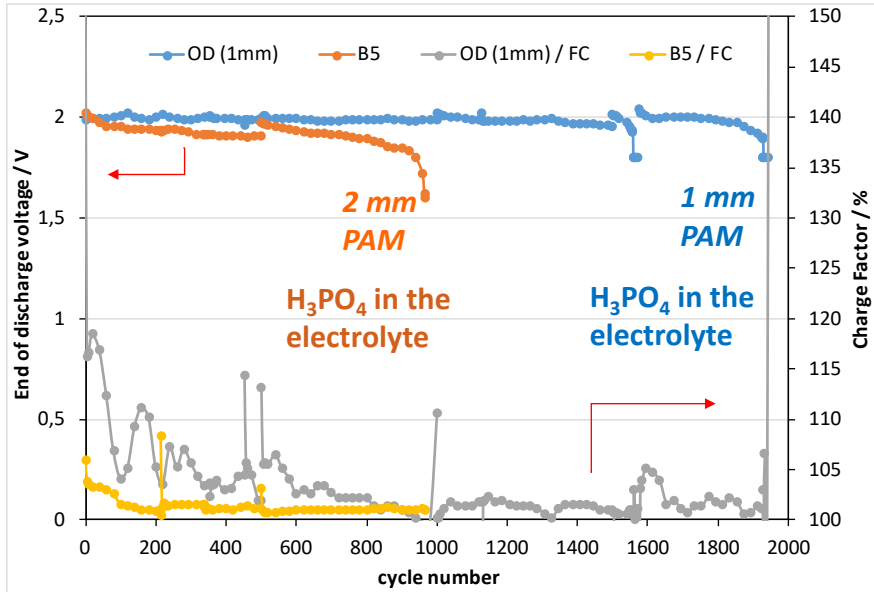
- The effect of the Poly-vinylphosphonic acid as PAM additive is rather adverse when the electrolyte is not doped
- The addition of H<sub>3</sub>PO<sub>4</sub> to the electrolyte increases the cycle life roughly 5 times
- The cell compression readjustment restores only a fraction of the electrode capacity for a short duration indicating that the loss of the contact between the PAM particles is not the primary phenomenon causing the loss of PbO<sub>2</sub> electrochemical activity
- The evolution of the impedance indicates the progressive development of resistive interfaces (capacitance loops) and accumulation of resistive PbO<sub>2</sub> with small number of defects (ohmic resistance shift)

# CYCLE AGEING OF THICK ELECTRODES WITH CALCIUM PHOSPHATE ADDED TO PAM



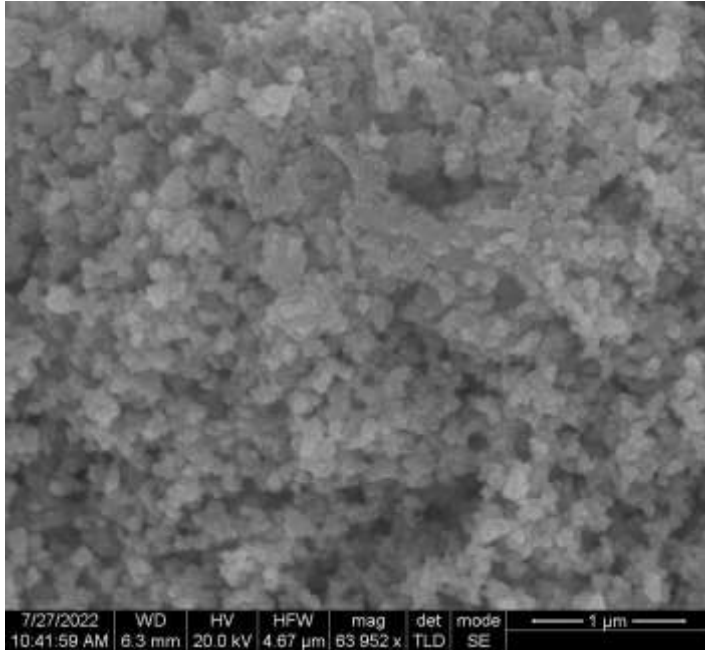
- The effect of the CaHPO<sub>4</sub> as a sole PAM additive is similar to those of the PVPA
- The addition of H<sub>3</sub>PO<sub>4</sub> to the electrolyte also increases the cycle life roughly 5 times, however the overall cycle life approaches 1000 cycles @  $\eta_{PAM} = 15\%$
- The cell compression readjustment effect is also similar, restoring the PAM utilization slightly above 30%
- The more significant initial increase of the ohmic impedance coincides with the initial loss of PbO<sub>2</sub> electrochemical activity suggesting the accumulation of resistive PbO<sub>2</sub> with small number of defects

# CYCLE AGEING OF THINNER ELECTRODES WITH CALCIUM PHOSPHATE ADDED TO PAM

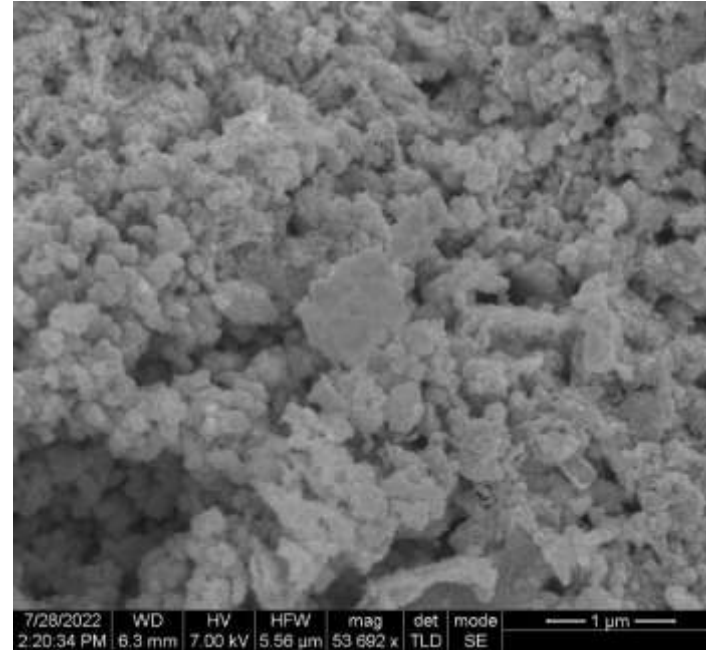


- The decrease of the electrode thickness slows down the ageing of PAM significantly
- The observed effect indicates that the electrolyte diffusion is linked with the accumulation of PbO<sub>2</sub> with poor electrochemical activity, i.e. PAM locations with poor access to H<sub>2</sub>SO<sub>4</sub> degrade faster
- The increase of the impedance is focused in the low-frequency domain indicating the development of resistive interfaces instead of accumulation of resistive PbO<sub>2</sub> with low amount of defects

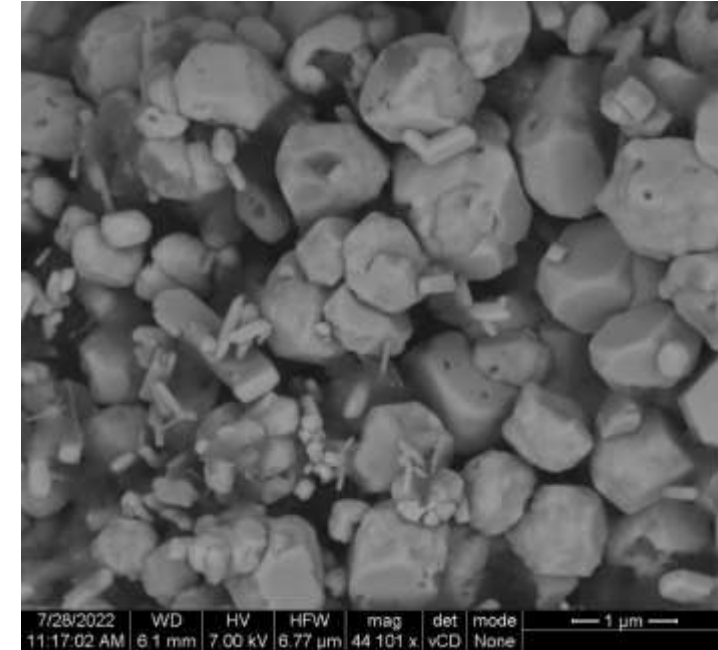
# IMPACT OF THE ADDED PHOSPHORIC ACID ON THE PAM MORPHOLOGY



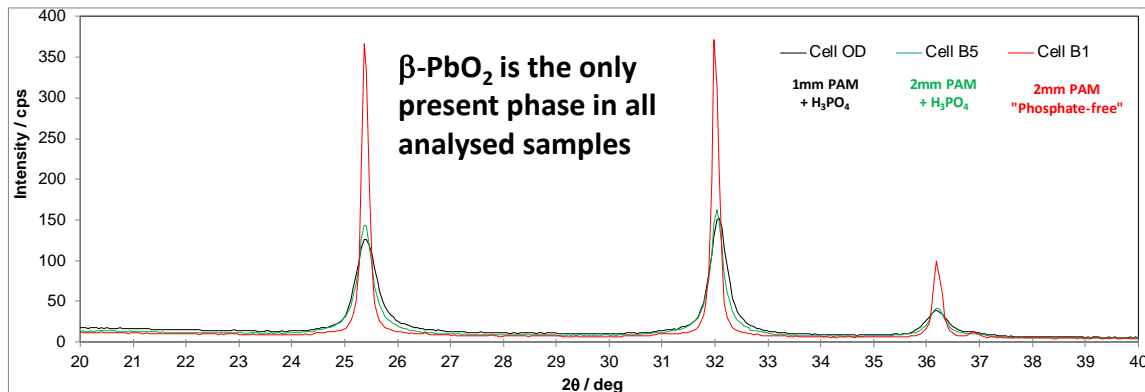
1 mm PAM (cell OD)  
 $H_3PO_4$  in the electrolyte



2 mm PAM (cell B5)  
 $H_3PO_4$  in the electrolyte



2 mm PAM (cell B1)  
"Phosphates-free" cell



- The presence of  $H_3PO_4$  in the formation electrolyte decreases the PAM particle size significantly
- The morphology and the phase composition of the thick and the thin electrodes is identical indicating that the PAM ageing process (capacity loss and increase of the impedance) proceeds also at submicron level

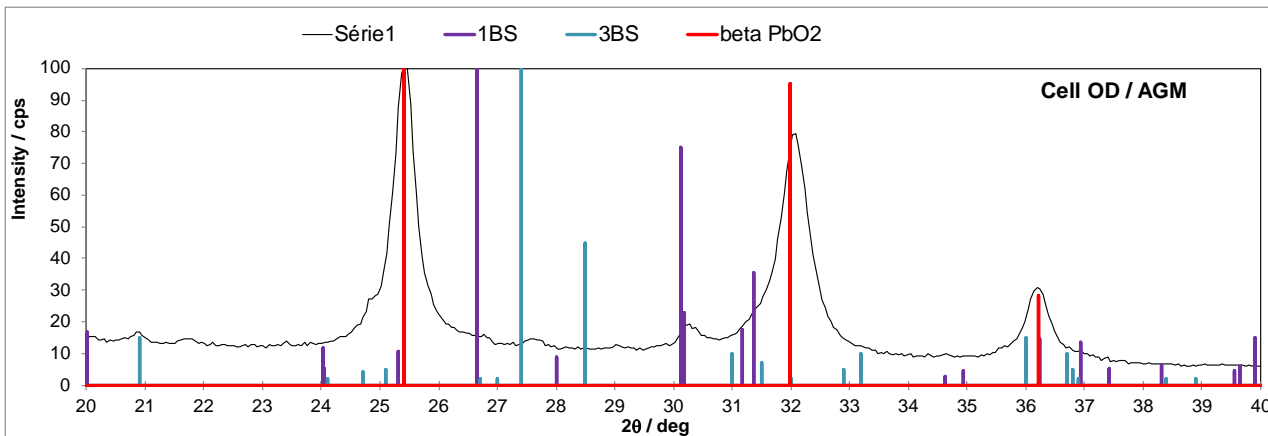
# IMPACT OF THE CYCLE AGEING ON THE ELECTRODE INTEGRITY



AGM separator facing the positive electrode (considerable penetration of PAM particles in the separator media)

Ti-SnO<sub>2</sub> current collector (after PAM detachment)

Pasting paper



- The visual inspection of the electrodes during the tear-down analysis showed that significant amount of PbO<sub>2</sub> penetrates the AGM (partial PAM softening)
- The restriction of this process by using more rigid porous layers (e.g. tubular gauntlet fabric) between the AGM and PAM should slow down further the ageing of the positive electrodes

## CONCLUSIONS

- The cycling behavior of Ti-SnO<sub>2</sub> / PAM electrodes formed in electrolyte containing H<sub>3</sub>PO<sub>4</sub> has been studied electrochemically and structurally
- The results from the electrochemical tests showed that addition of 1% H<sub>3</sub>PO<sub>4</sub> to 1.15 s.g. H<sub>2</sub>SO<sub>4</sub> for jar formation results in “activation” process delivering electrodes with improved PAM utilization and long cycle-lifetime
- The benefits from this “activation” phenomenon increase considerably when the electrode thickness is lower indicating that the PAM degradation is linked with the H<sub>2</sub>SO<sub>4</sub> diffusion process
- The tear down analysis of the aged electrodes showed that PAM is comprised entirely of β-PbO<sub>2</sub> with a particle size decreasing significantly in the presence of H<sub>3</sub>PO<sub>4</sub>
- The visual observation of the electrodes showed that considerable amount of β-PbO<sub>2</sub> passes across the pasting paper and penetrates inside the AGM, explaining only a fraction of capacity loss together with the decrease of the cell stack compression along the cycling
- The analysis of the whole ensemble of electrochemical impedance spectra indicates indirectly that the performance of the Ti-SnO<sub>2</sub> current collectors does not degrade substantially during the cycle aging



## ACKNOWLEDGEMENTS

This work has been realized in association with INES.2S within the French national program Investments for the Future (ANR-10-IEED-0014-01)

The authors would like to thank the companies which provided free of charge materials used to built electrodes and cells



AGM separators



Pasting paper



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