

Impact of PAM Charge Potential, SoC Recovery Levels and Relaxation Time on SoF Performance During Charge Recovery Testing

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Hammond Group Inc.

Session: CR2 - Charge Recovery [part 2: optimizations]

Workshop on Automotive Lead Battery Advancements

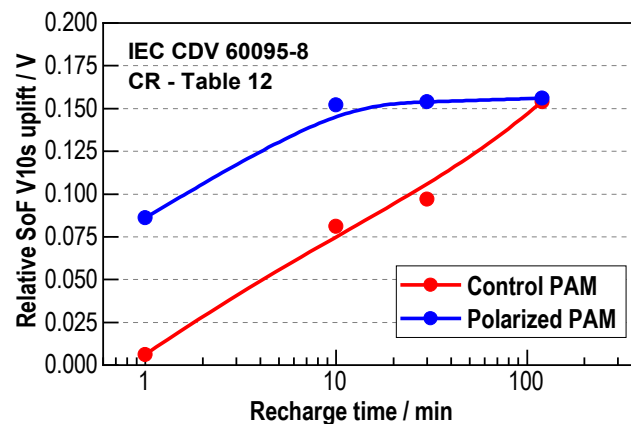
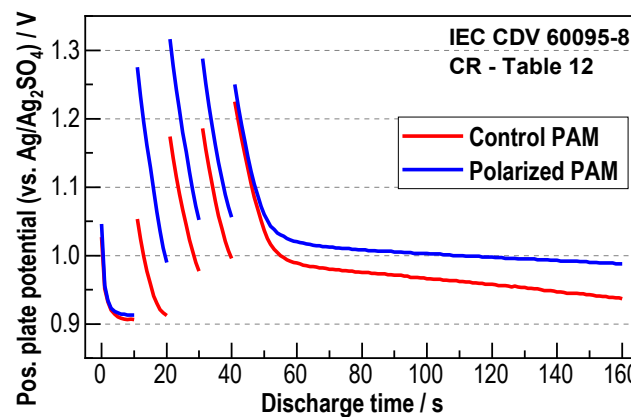
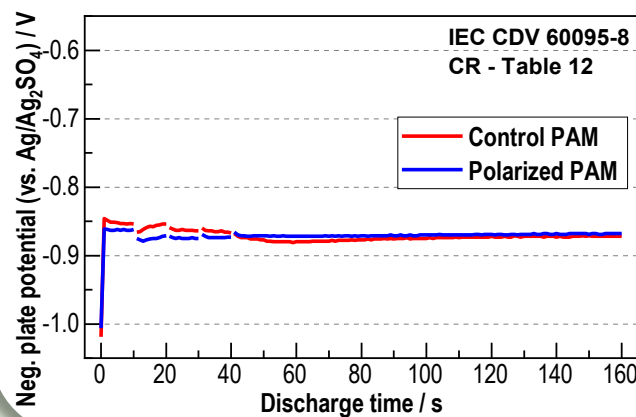
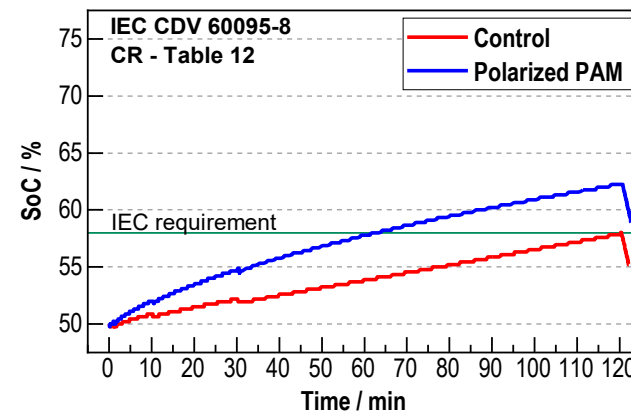
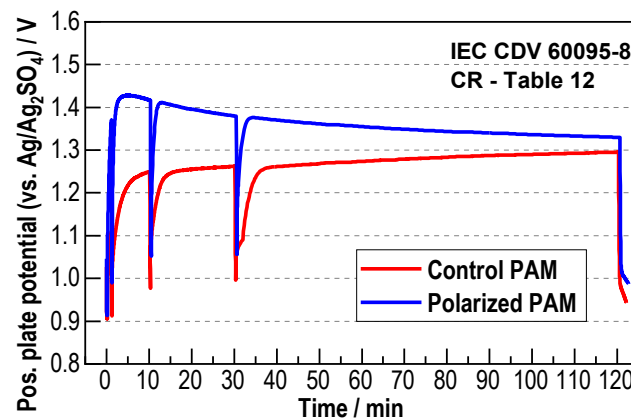
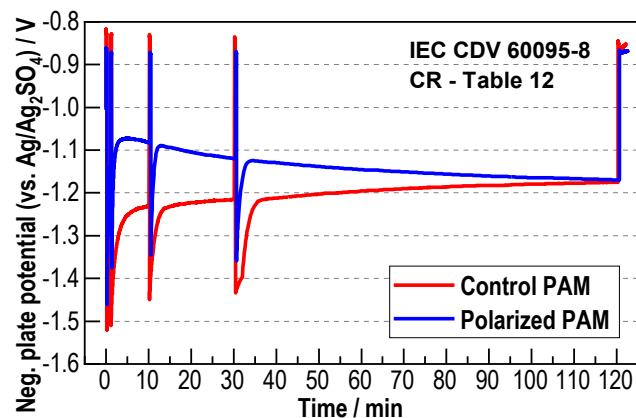
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Impact of PAM Charge Potential, SoC Recovery Levels and Relaxation Time on SoF Performance

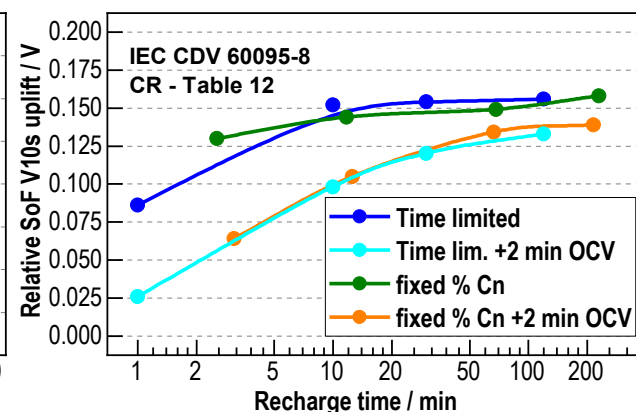
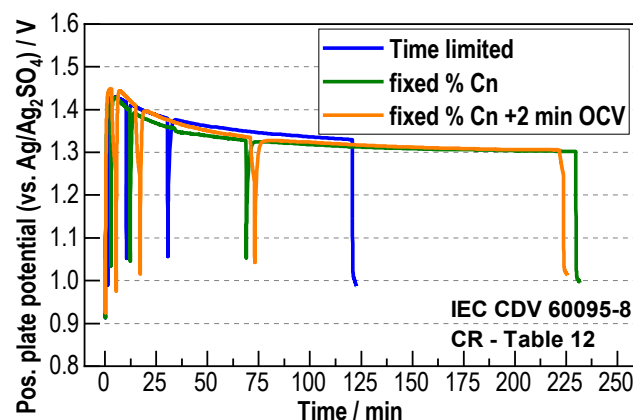
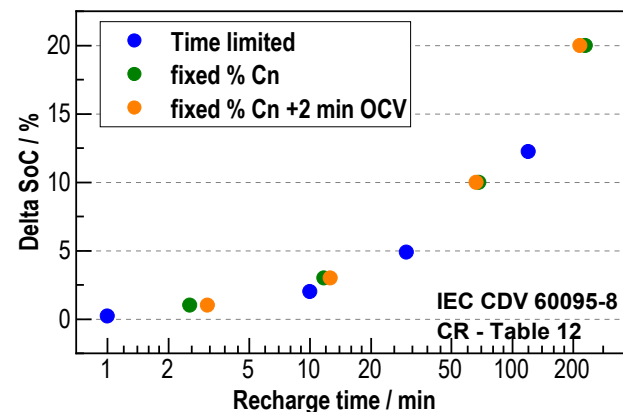
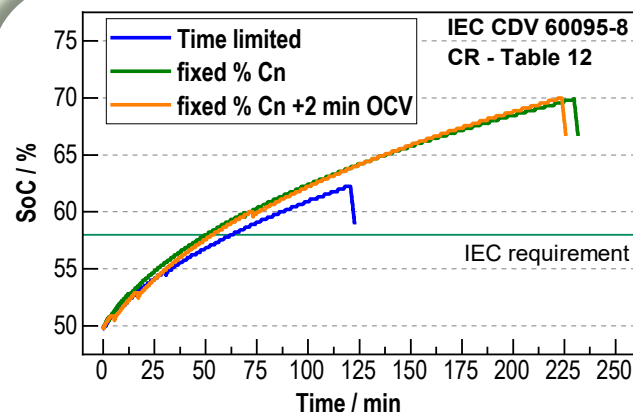
During Charge Recovery Testing

Plamen Nikolov, *Institute of Electrochemistry and Energy Systems – Bulgarian Academy of Sciences*

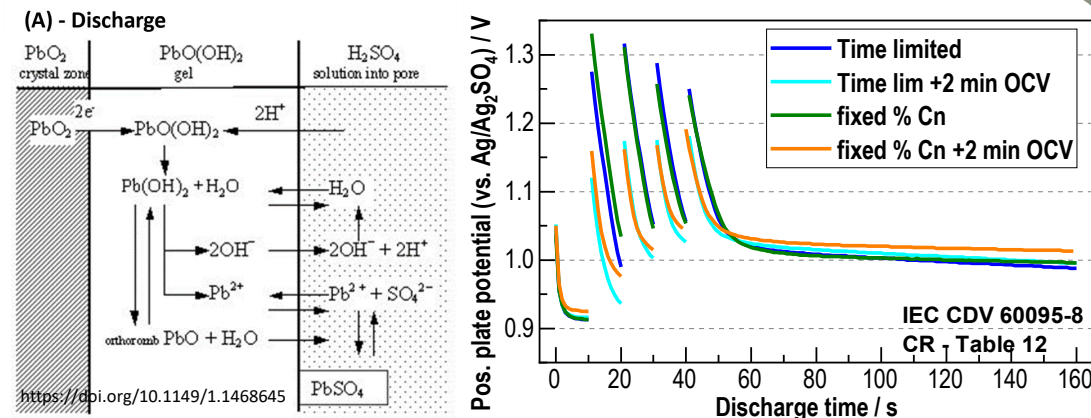
- Test cell: flooded 2 V / 4.5 Ah; 2 positive / 3 negative plates. Charge Recovery testing according to IEC CDV 60095-8 - Table 12.
- **Study case #1:** Increased PAM potential during charge by modification of NAM expander recipe – standard vs. improved (Hammond Group).
- **Study case #2:** Effect of SoC recovery levels on SoF – time limits 1, 9, 30, 90 min. are substituted by 1, 3, 10, 20% Cn return.
- **Study case #3:** Impact of relaxation time on CR SoF – introduction of 2 min. OCV before SoF discharge step.



- Change of NAM expander recipe allows elevated PAM potential during charge.
- Significant 50% improvement vs. control cell for SoC recovery was registered.
- PAM potentials during SoF surge substantially in the case of polarized PAM.
- More PAM polarization during charge provokes significant increase of SoF voltage uplift.



- The SoC recovery trend is very similar for time limited and % Cn return profiles.
- SoC accumulation depend on charging time and follows exponential trend.
- Charging times longer than 10 min. lead to marginal increase of SoF voltage uplift.
- Relaxation time has substantial negative impact on SoF voltage uplift.



Slope: Interfacial charge storage or change of ion equilibrium at surface/solution interface
Plateau: transformation of one phase to another phase

- The relaxation time changed the chemical/structural features of PAM/solution interface and diffusion processes which result to suppression of pseudocapacitive behavior and facilitate formation of PbSO_4 phase.

Key message: PAM polarization during charge has more beneficial impact on SoF pseudo-capacitance than SoC recovery levels (charging time). Relaxation time before SoF provokes chemical/structural changes suppressing PAM pseudo-capacitance.

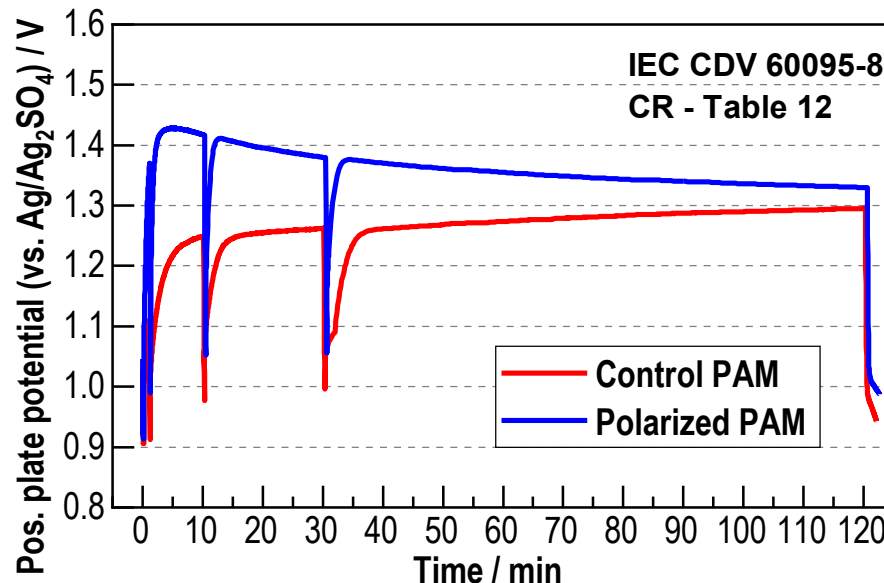
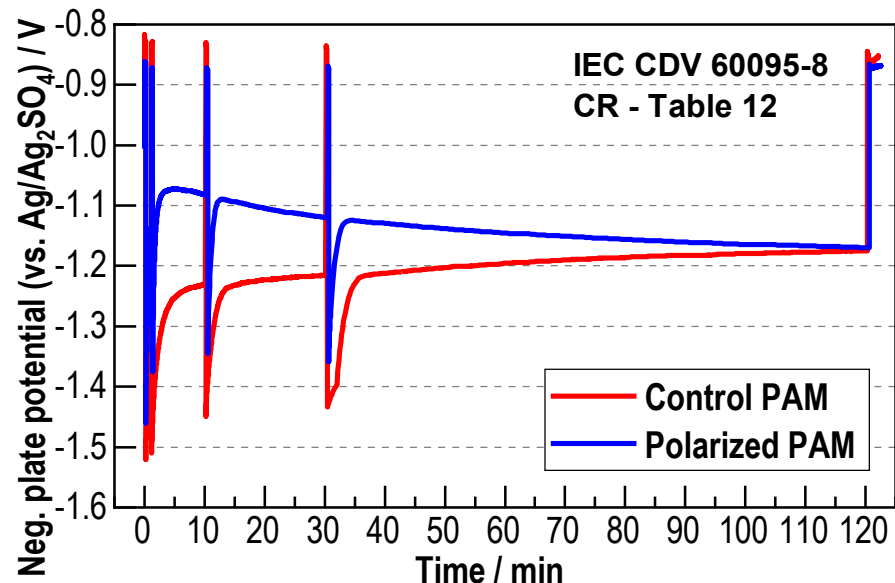
Thank you for your attention!

Acknowledgement: The research team of the Lead-Acid Batteries Department at IEES-BAS acknowledges with gratitude the financial support provided by **Consortium for Battery Innovation (USA)** and **Hammond Group Inc. (USA)** for implementation of the present study. We want to express our sincere thanks to **Dr. Eckhard Karden** and **Dr. Matt Raiford (CBI)** for encouraging this research and for their valuable comments.

Scope of the study and experimental set-up

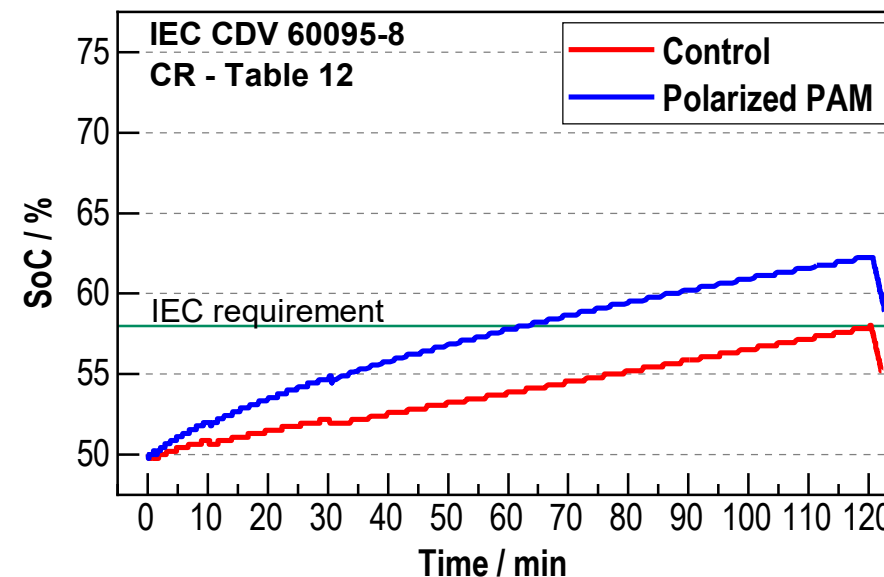
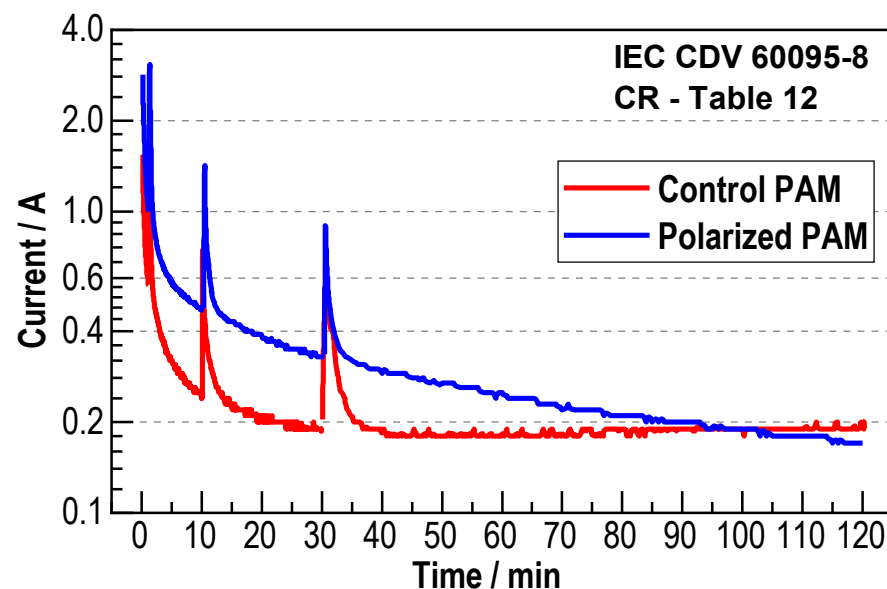
- PAM and NAM recipes: identical for all test cells.
- Expander formulation provided by Hammond Group Inc.: standard vs. improved
- Test cell: 2 V / 4.5 Ah; 2 positive / 3 negative plates; Flooded; PE pocket separator.
- Charge recovery testing according to IEC CDV 60095-8 - Table 12.
- Before charge recovery testing all cells undergo the following sequence: C20-CCA-C20-CCA-C20-CCA.
- **Study case #1:** More PAM voltage polarization during CR charge steps by modification of NAM expander recipe - standard vs. improved).
- **Study case #2:** Effect of CR SoC recovery levels on SoF performance – time limits 1, 9, 30, 90 min. are substituted by 1, 3, 10, 20% Cn return.
- **Study case #3:** Impact of relaxation time on CR SoF performance – introduction of 2 min. OCV before SoF.
- Charge recovery tests are executed sequentially on two streams of cells: study case #1 and #3 and study case # 2 and #3.

Study case 1 – SoC recovery

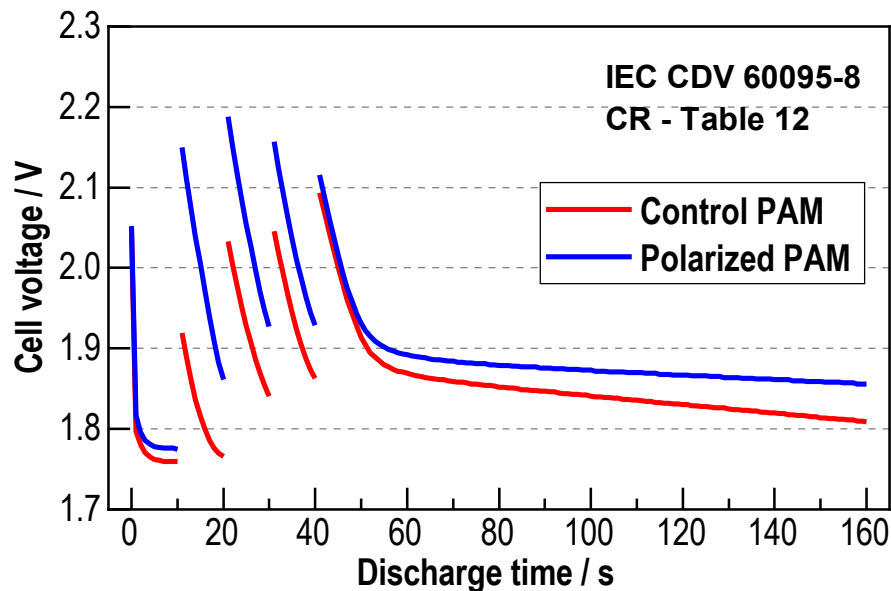


- The improved expander formulation allows charging of NAM at considerably lower potentials.
- PAM potential reaches values of 1.35 V (vs. Ag/Ag₂SO₄) or more even above 1.40 V during the first 20 min of charge compared to control PAM which exhibit values of 1.25-1.30 V.

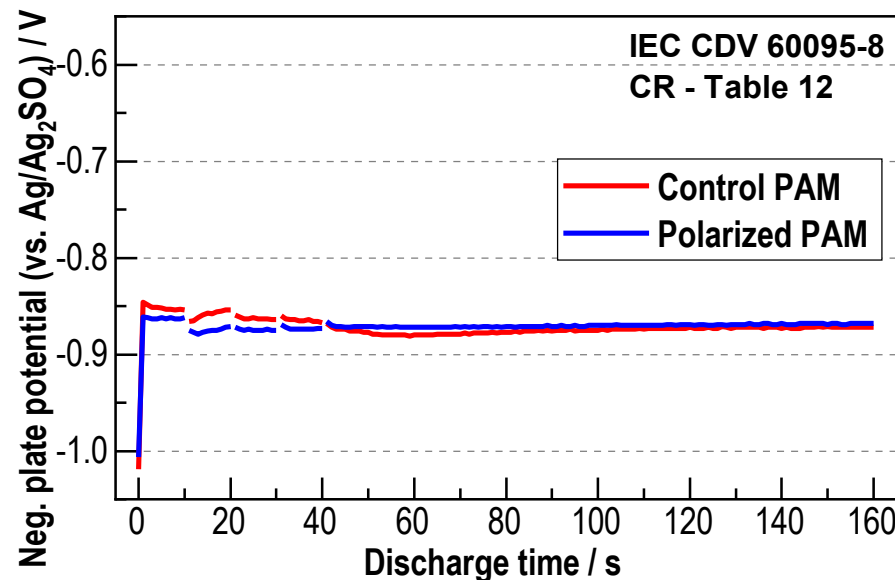
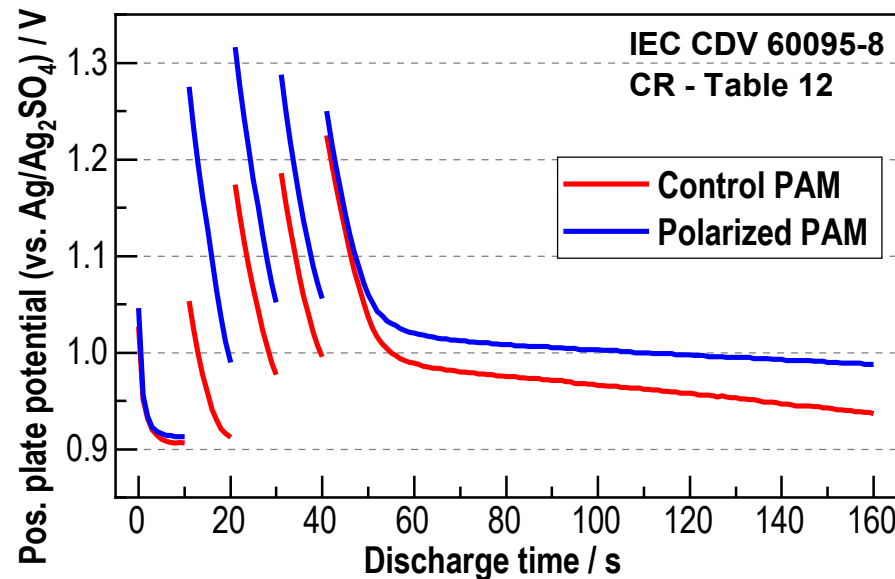
- The higher voltage polarization levels of PAM during charge yields to noticeable increase of charging current (up to 2 times).
- The control cell has SoC recovery of 8% while the cell with more polarized PAM reaches SoC recovery of 12% or 50% improvement vs. control.



Study case 1 – SoF performance

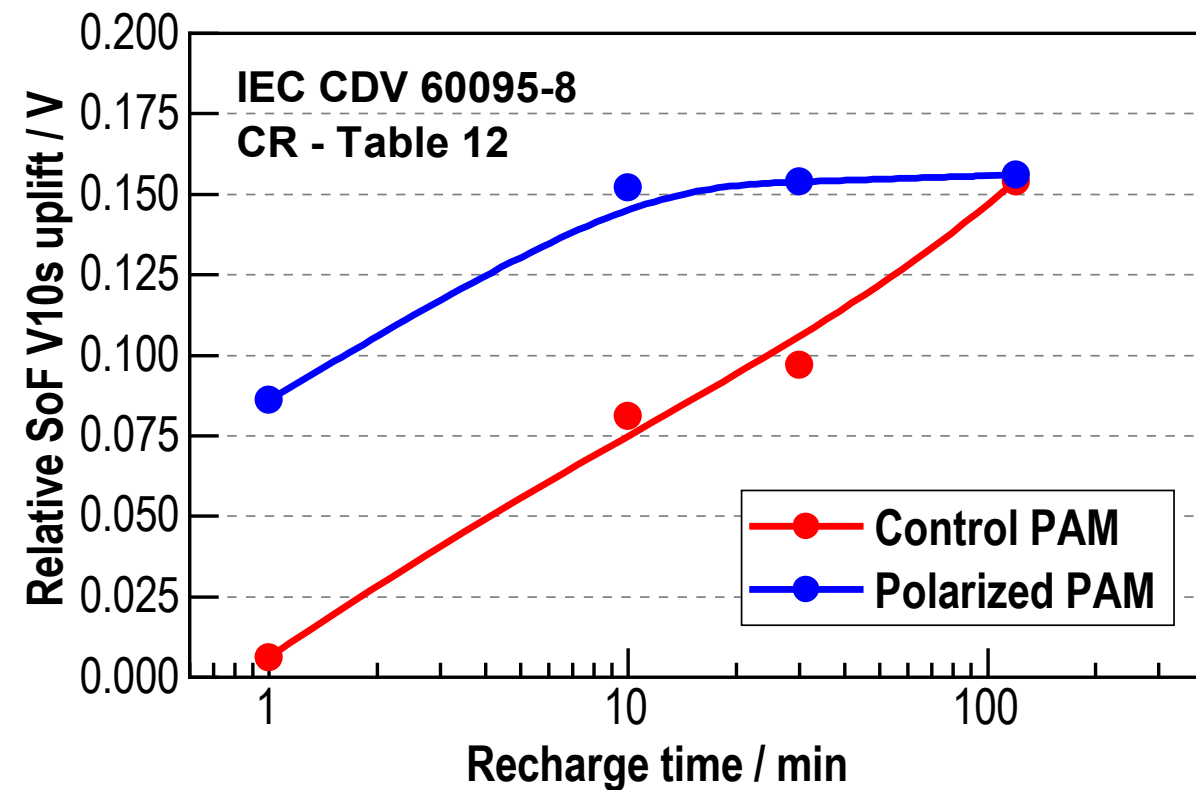
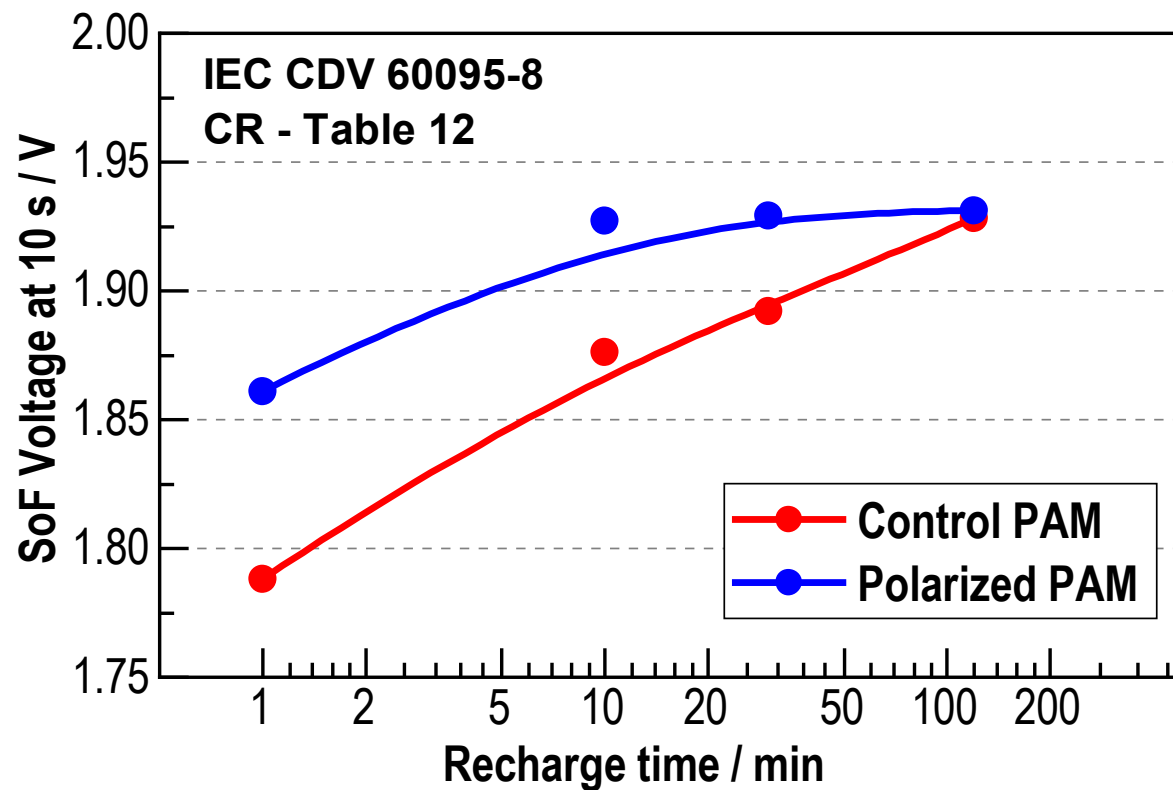


- The PAM potential response during SoF fully determines the cell voltage.
- Higher PAM potential during charging results to remarkable increase of SoF cell voltage.



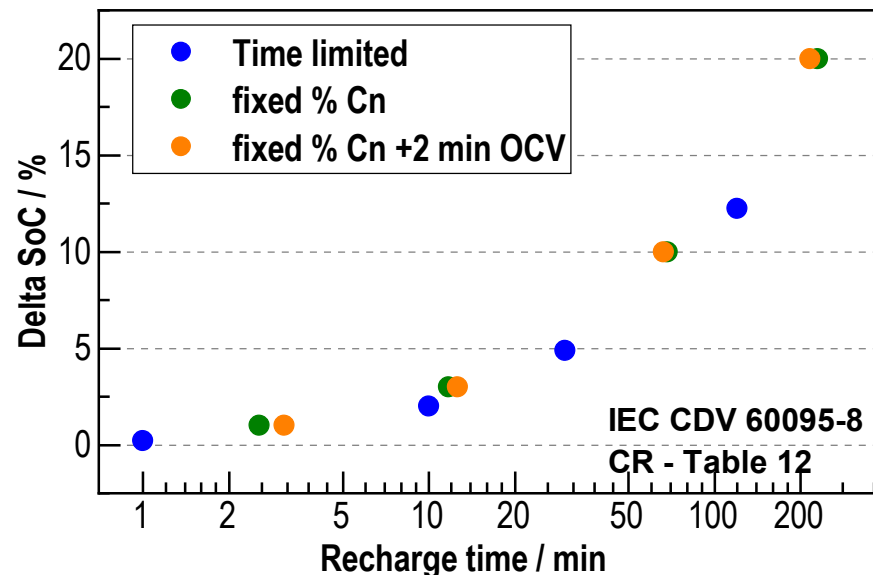
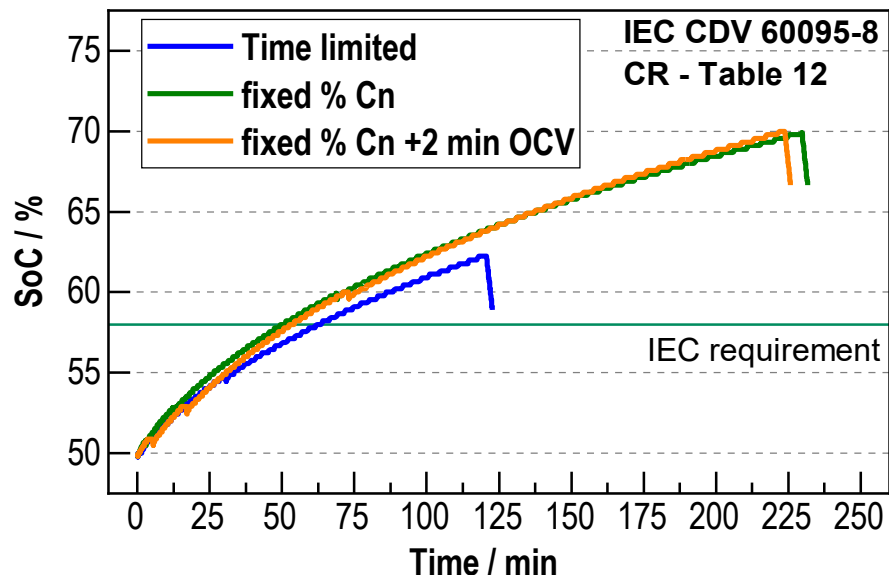
- PAM potential values at beginning and at the end of SoF discharge surge substantially in the case of polarized PAM.
- During the 10 s SoF discharges PAM potential spans more 250 mV for polarized PAM (even after 1 min recharge) while for control PAM less than 200 mV.
- The voltage course of the plateau is also affected but not the trend of steep slope.
- The change of expander formulation does not have any impact on NAM potential values during SoF discharge.

Study case 1 – SoF performance



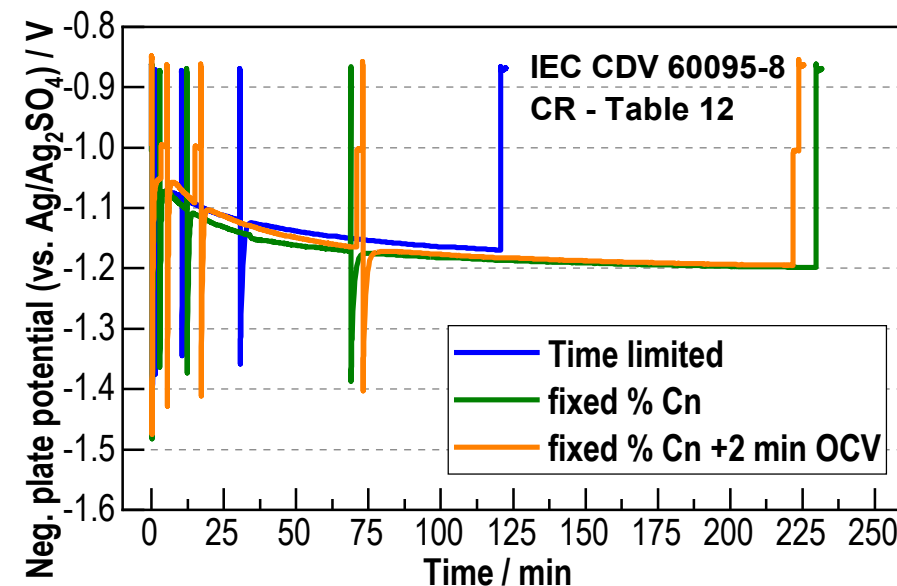
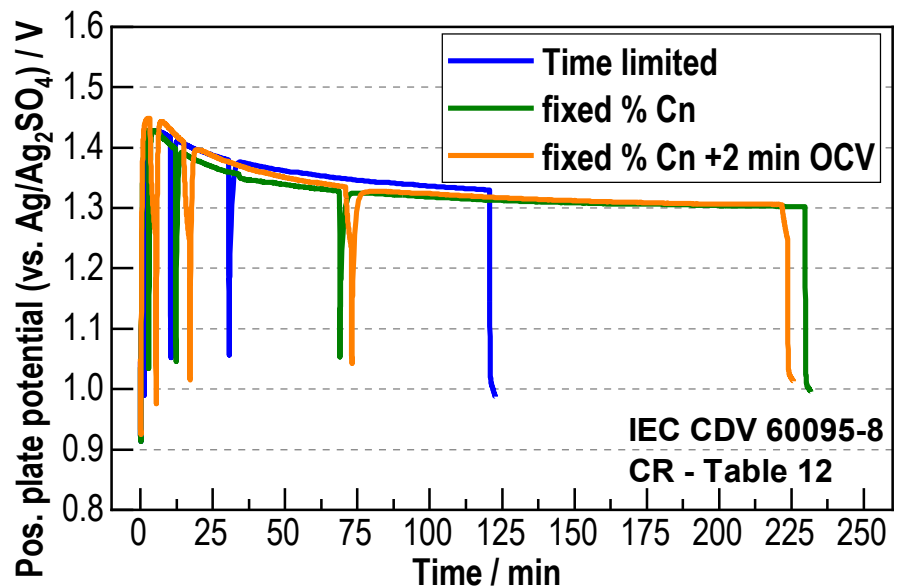
- Elevated PAM polarization during CR charging results to considerable shift of SoF absolute voltage values and relative voltage uplift to unusually higher values.
- The impact of PAM polarization is very strong for charging times less than 30 min while above 30 min the influence of PAM polarization disappears.

Study case 2 & 3 – SoC recovery

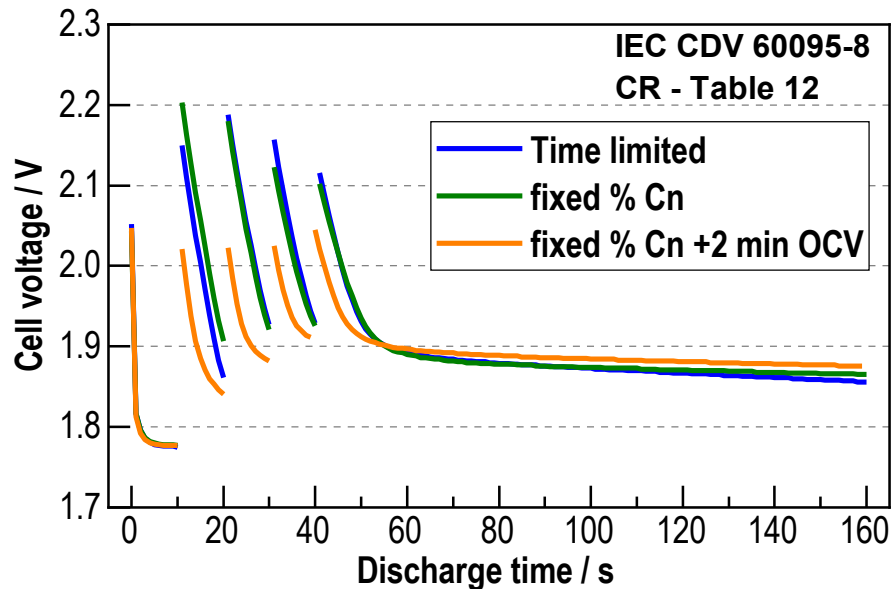


- The fixed % Cn return profile has about twice longer duration compared to the time limited CR.
- OCV steps have no impact on SoC recovery
- SoC recovery is very similar despite the minor difference in the trends for time limited and fixed % Cn return cell.
- SoC accumulation depend on charging time and follow exponential trend.

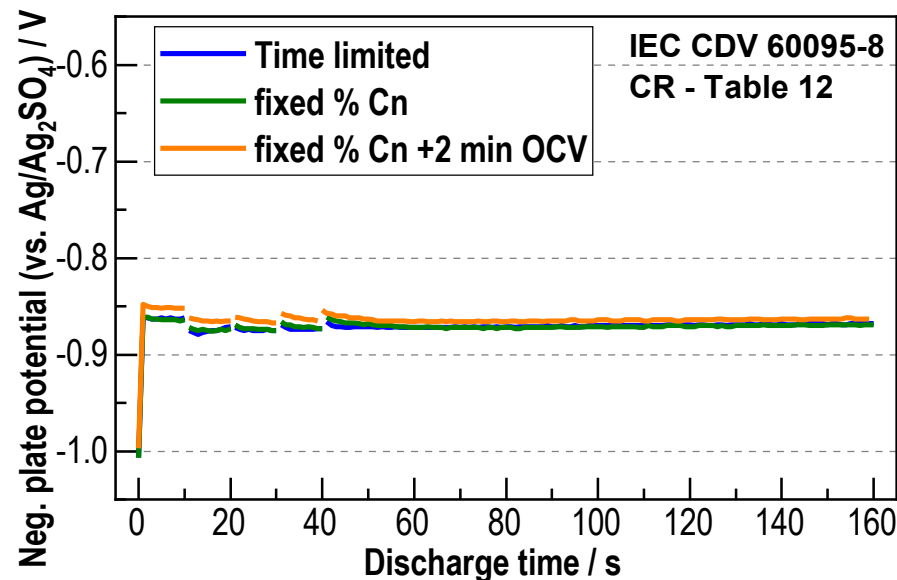
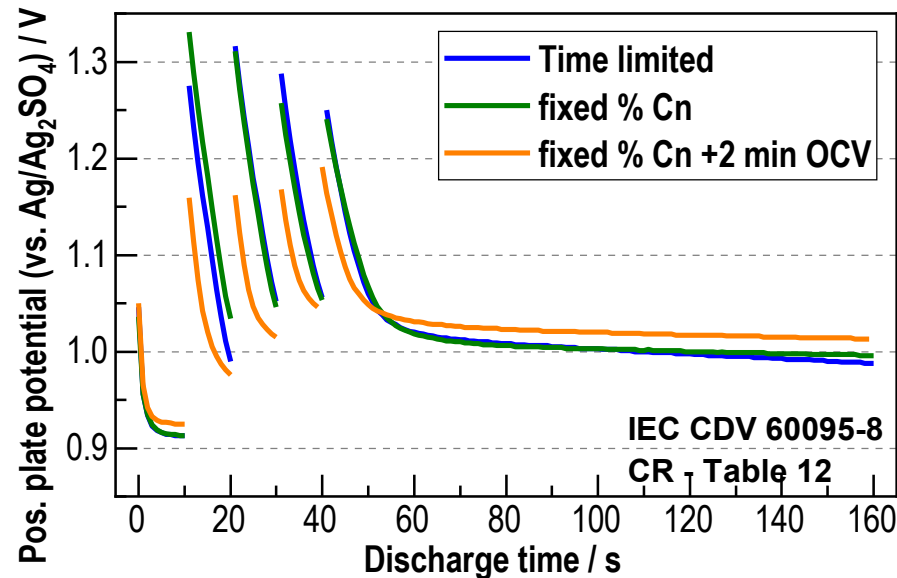
- SoF events are happening at varying time moments.
- PAM and NAM potentials during charging follow identical trend of change both for time limited and fixed % Cn return.
- The incorporated OCV steps do not affect the PAM and NAM potentials during charge.



Study case 2 & 3 – SoF performance

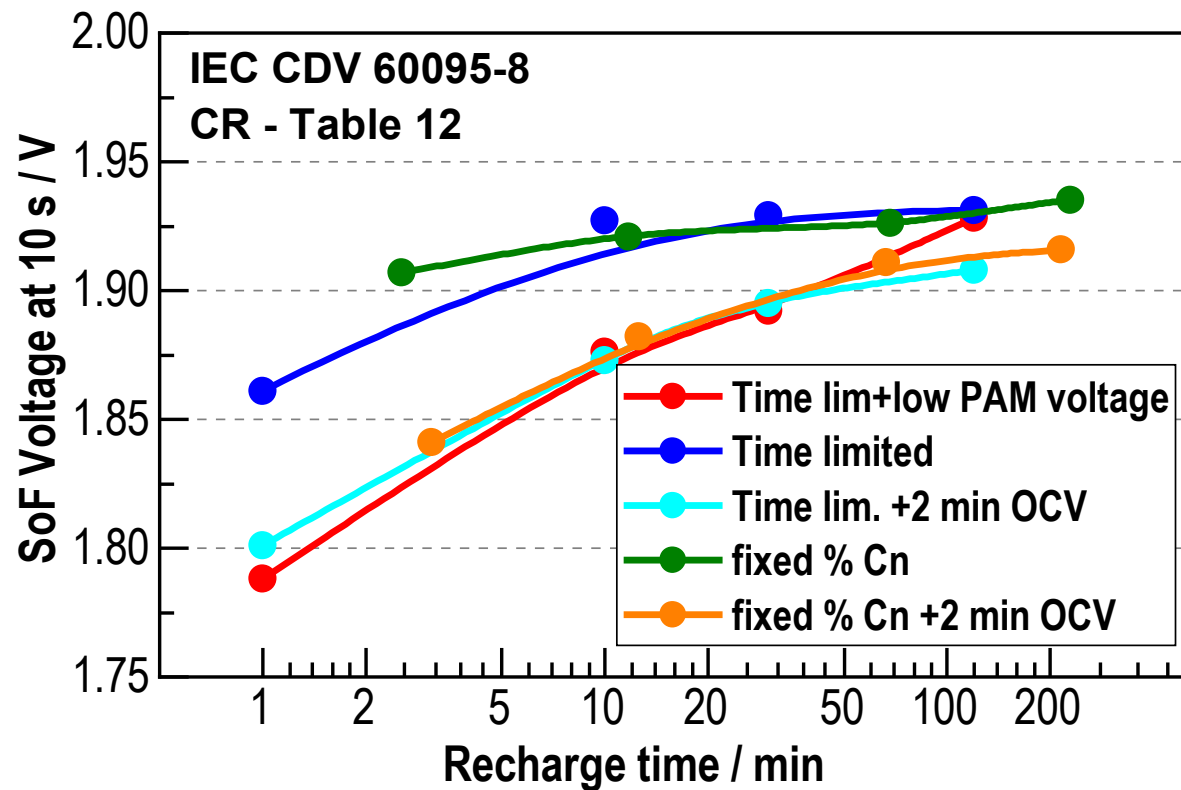


- The PAM potential response during SoF fully determines the cell voltage.
- Higher PAM potential during charging results to remarkable increase of SoF cell voltage.
- Extended charge time, increased SoC recovery level and introduction of relaxation period have no any impact on NAM potential during SoF.

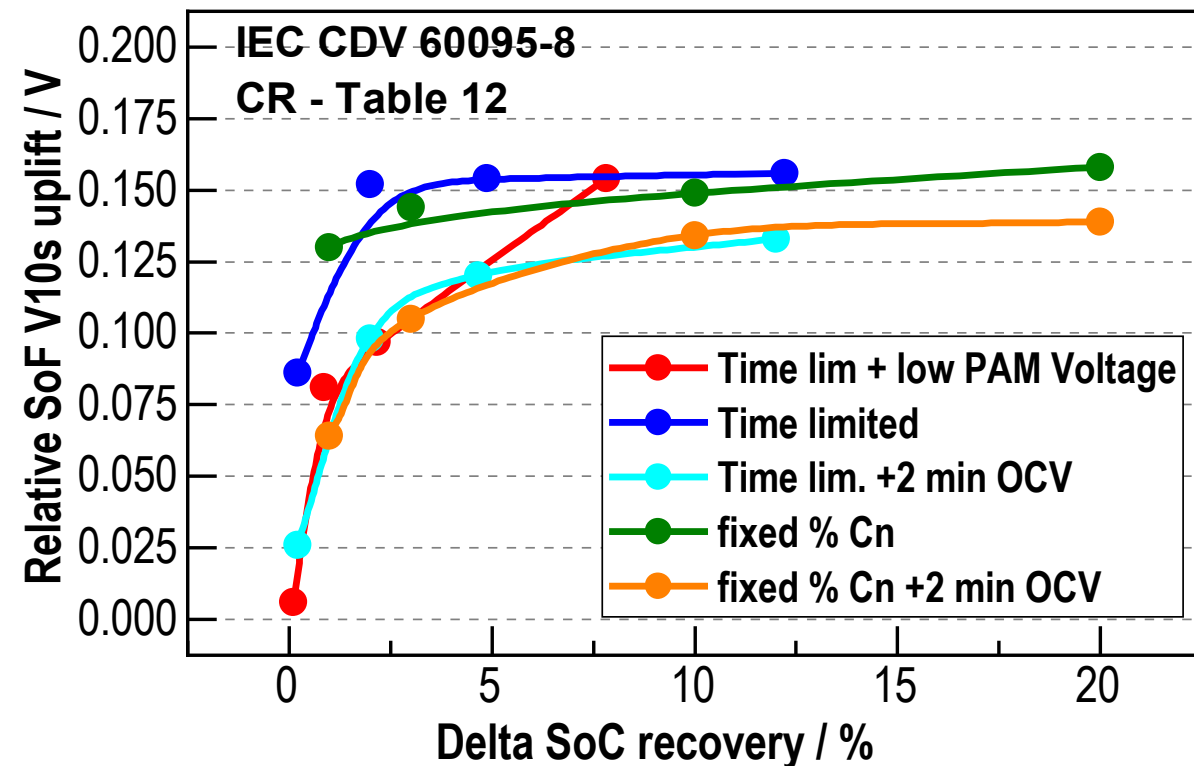


- The prolonged time of the first charge step in the case fixed % Cn return results to further shift of PAM potential to higher values during SoF discharge but the swing between max and min value is 250-300 mV similar to Time limited cell.
- Further extend of SoC recovery has no impact on PAM SoF performance.
- Introduction of relaxation time before SoF discharge has substantial negative impact on PAM potential by shifting it to lower values and reduce the max to min span to 150-200 mV.
- Interesting observation is that relaxation time leads to slight uplifted SoF discharge plateau.

Study case 2 & 3 – SoF performance



- It can be seen that absolute cell voltage values at the of SoF discharge follow logarithmic trend increase as function of charging time during CR.
- Charging times longer than 10 min. lead to marginal increase of SoF cell voltage values.
- The phenomena occurring during relaxation period before SoF have substantial negative impact by shifting voltage with 30-60 mV to lower values especially for charging times smaller than 30 min.

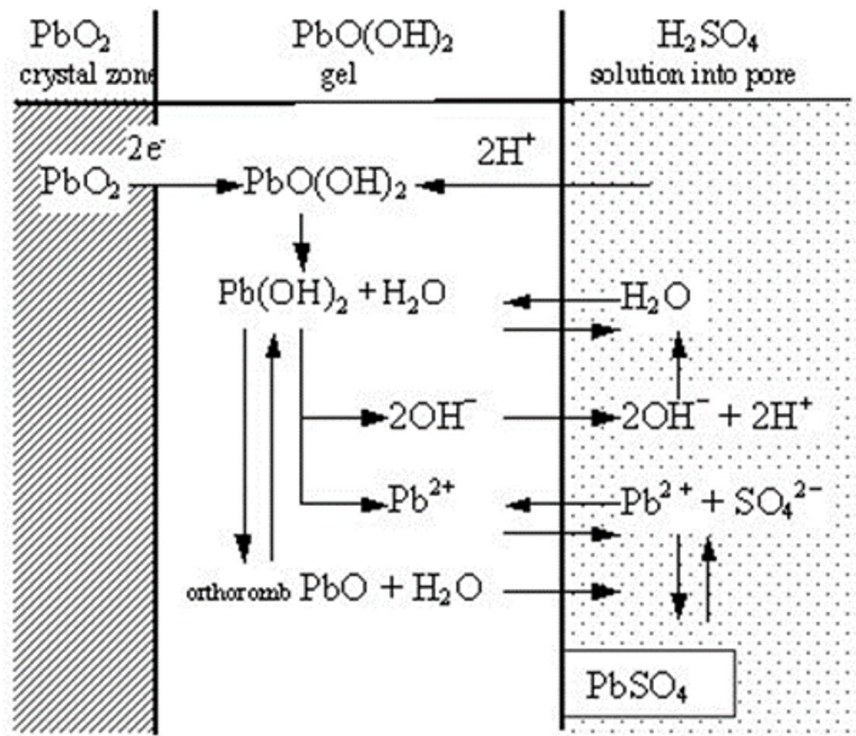


- PAM potential during charge has more beneficial impact on SoF pseudo-capacitance than SoC recovery levels (charging time)
- When PAM potential has adequately high values only 10-12 min. of charging or 2-3 % SoC recovery is sufficient to ensure substantial SoF voltage uplift.

Phenomena responsible for voltage slope and plateau

(A) - Discharge

<https://doi.org/10.1149/1.1468645>

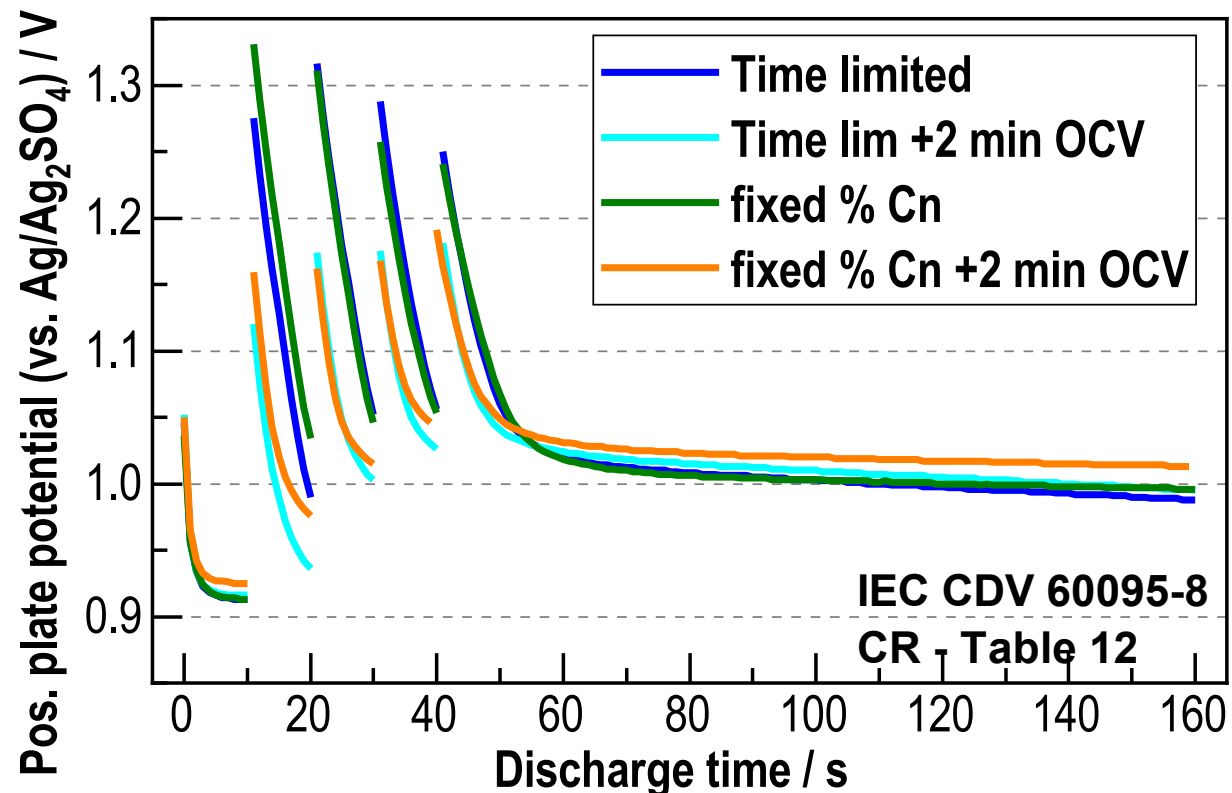


Slope:

Interfacial charge storage or change of ion equilibrium at surface/solution interface

Plateau:

transformation of one phase to another phase



- The relaxation time before SoF discharge provokes considerable change in the chemical/structural features of PAM/solution interface and diffusion processes which result to suppression of pseudocapacitive behavior and facilitate formation of PbSO_4 phase.
- Introduction of relaxation time elevates PAM potential at the plateau at the same time the increased SoC recovery level/prolonged charging time (fixed % Cn return) change the slope to be more gradual (less steep).

KEY OUTCOMES

- The elevated PAM potential during charge has substantial beneficial impact on SoC recovery, SoF voltage uplift by enhancing the pseudo-capacitive behavior.
- Higher SoC recovery levels or prolonged charging steps during CR do not exhibit noticeable positive effect on SoF performance.
- Introduction of 2 min. relaxation time before SoF discharge has significant negative influence on voltage uplift.
- The relaxation time before SoF discharge changes in the chemical/structural features of PAM/solution interface and diffusion processes which result to suppression of pseudocapacitive behavior and facilitate formation of PbSO_4 phase.

THANK YOU FOR YOUR ATTENTION!

Acknowledgement

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