Smith Lab @ TU Delft

Photoelectrochemical redox flow battery: *Challenges and recent efforts*

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Introduction

Unbiased Solar-charging Redox Flow Battery

- Solar-charging redox flow battery (SRFB) is composed of **photoelectrochemical (PEC) charging** and **redox flow battery (RFB)** components which can generate electricity *via* reversible reactions.

$$A_{red} + B_{ox} \underset{\text{Discharging (RFB)}}{\overset{\text{Solar charging (PEC)}}{\rightleftharpoons}} A_{ox} + B_{red}$$

- Flexible capacity (*i.e.*, flexible resevior's volume) and low material cost ($30-80 per kWh).[1]

Challenges & Approaches

I. Chemical degradation under the light → **"Dark" PEC charging**

II. Low cell voltage & capacity → **Wide band-gap PEC device**

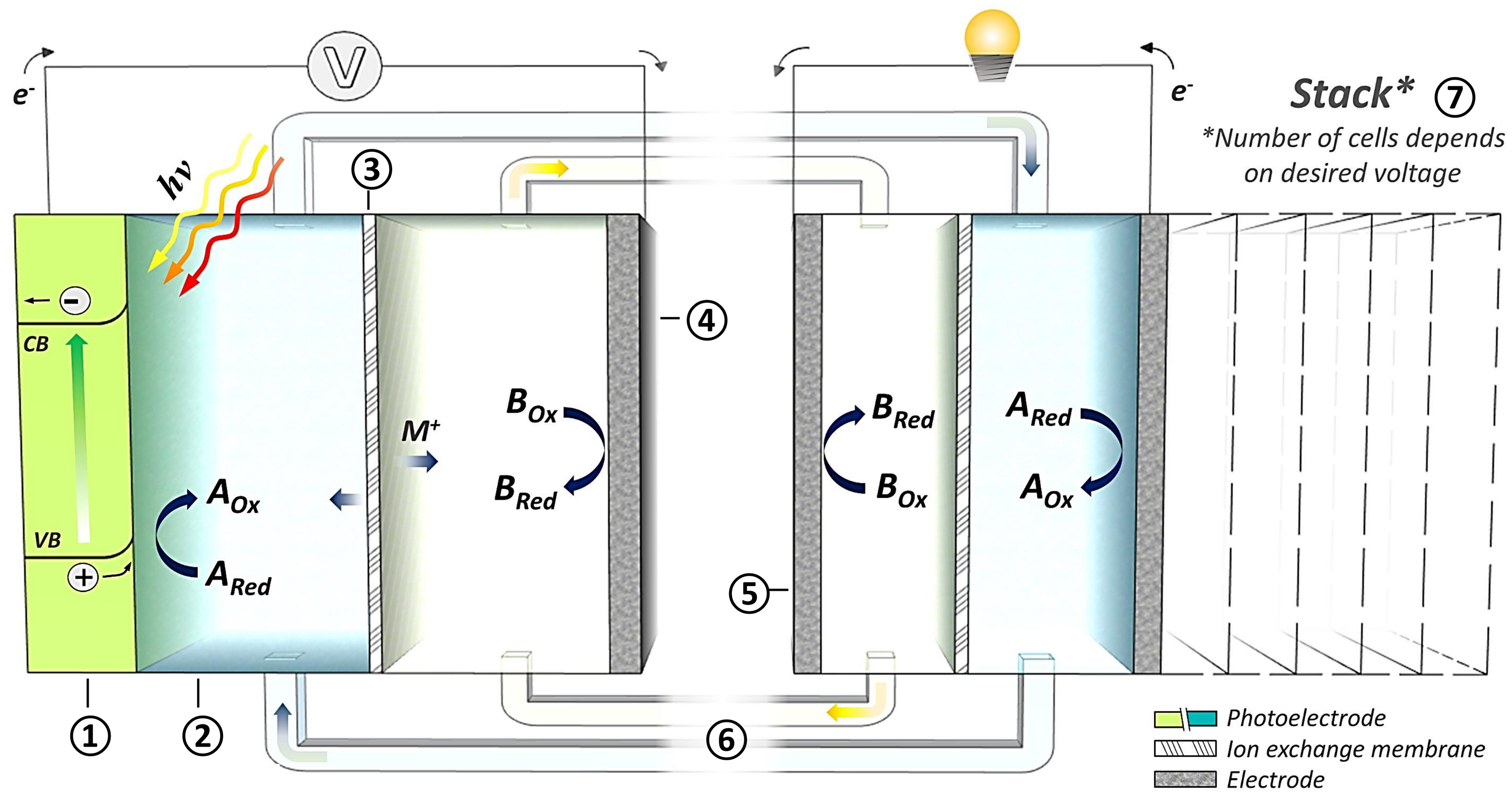
III. Competitive reaction with HER → **Use of Carbon or other non-Pt catalysts**

IV. Low specific capacity (~50 Wh/kg) → **Solubility tuning using organics**

Project overview

PEC charging part

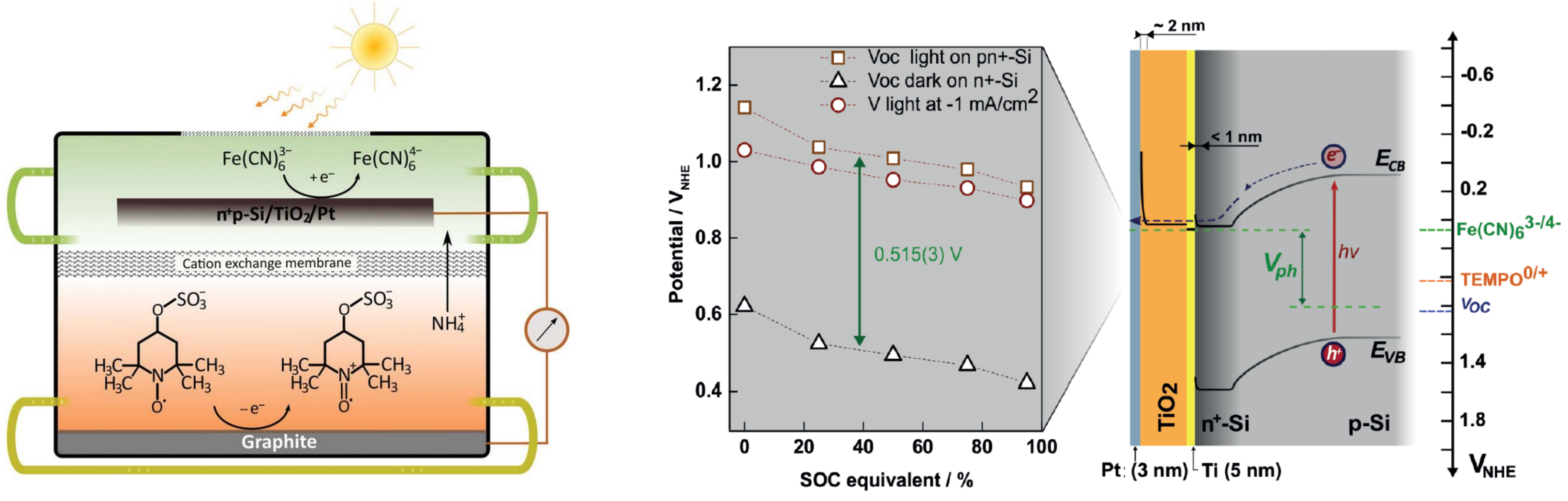
1) **PEC electrode:** can be n-type or p-type. *p-Si* and *p-GaP* have been used in this work.
2) **Electrolytes:** $Fe(CN)_6^{3-/4-}$ or AQS has been used as a catholyte and $TEMPO^{0/+}$ or NaI – as an anolyte.
3) **Membrane:** Nafion-117 (cation exchange) was used. Anion exchange membrane also can be applied in case of alkaline based electrolytes.
4) **Counter electrode:** Conducting carbon paper or Pt wire have been used.

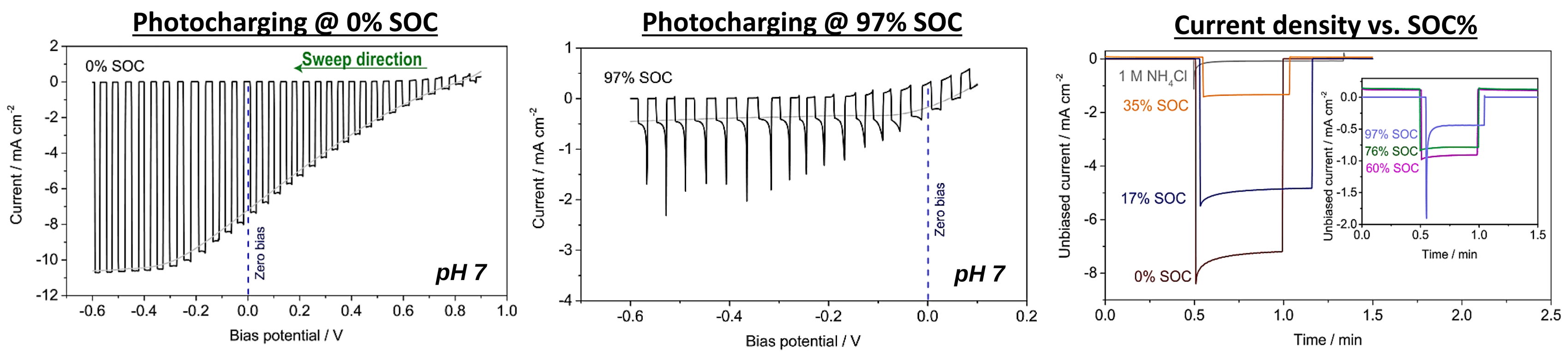


RFB discharging part

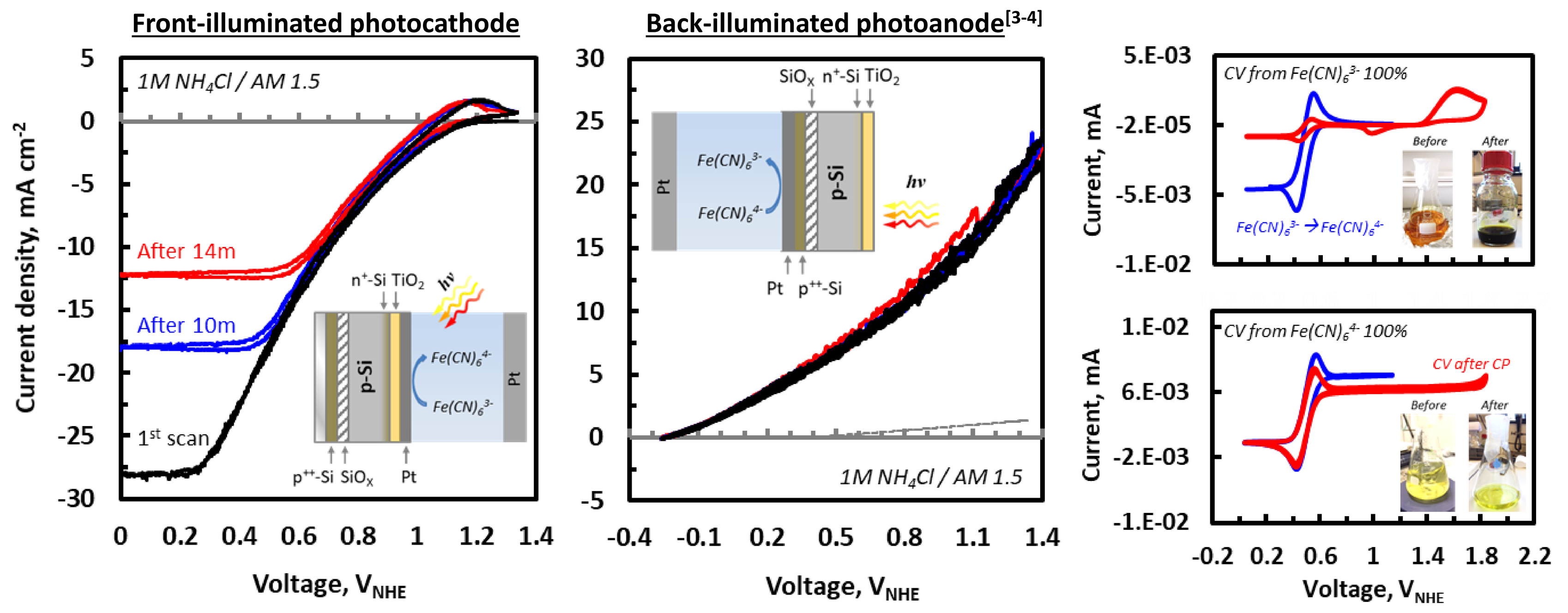
5) **RFB electrodes:** Commercial *Porto RFB cell* has been used in this study. *Au coated Cu plates* were used for both cathode and anode.
6) **Peristaltic pump:** Pumping rate of 70 mL/min with chemically durable Teflon and neoprene tubing.
7) **Cell stacking:** The stack voltage is the sum of single cell voltages (the current density is defined by the active area of a single cell). A single cell battery with 25 cm² active area was used in this work.

Challenge #1 *Chemical degradation under the light*



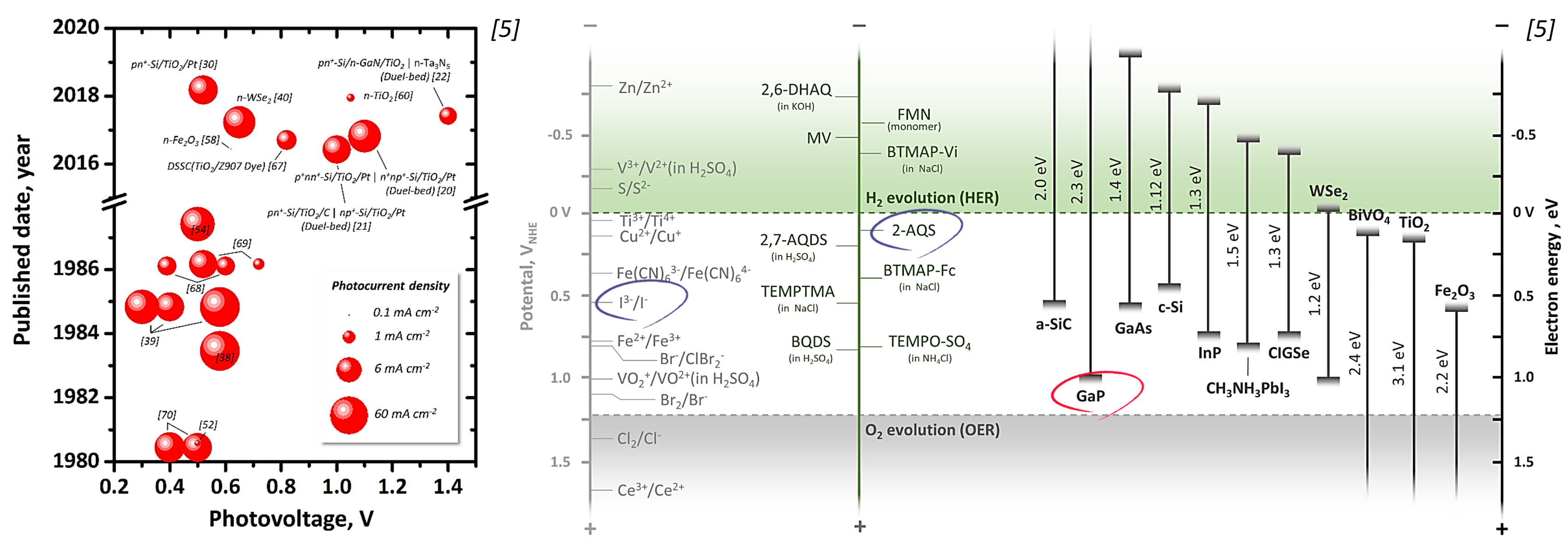


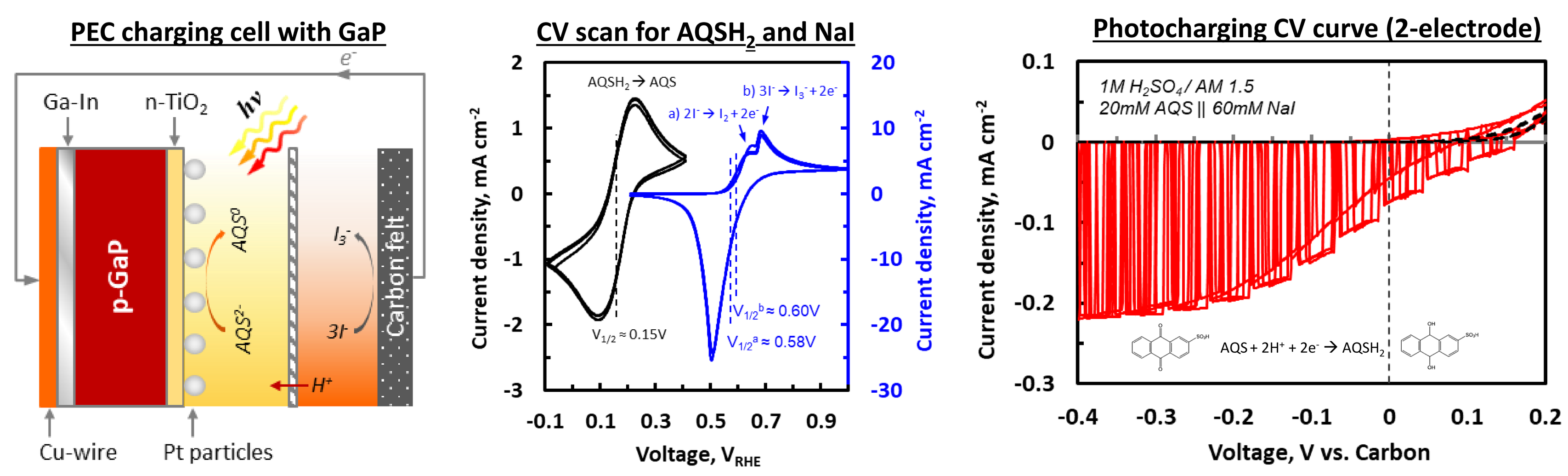
- TiO_2 covered pn⁺-Si with $V_{OC} \approx 0.52$ V. Both $Fe(CN)_6^{3-/4-}$ and $TEMPO^{0/+}$ are within band-edge of the c-Si [2].
- However, significant charging current decrease due to the $Fe(CN)_6^{3-/4-}$ coloration has been observed.



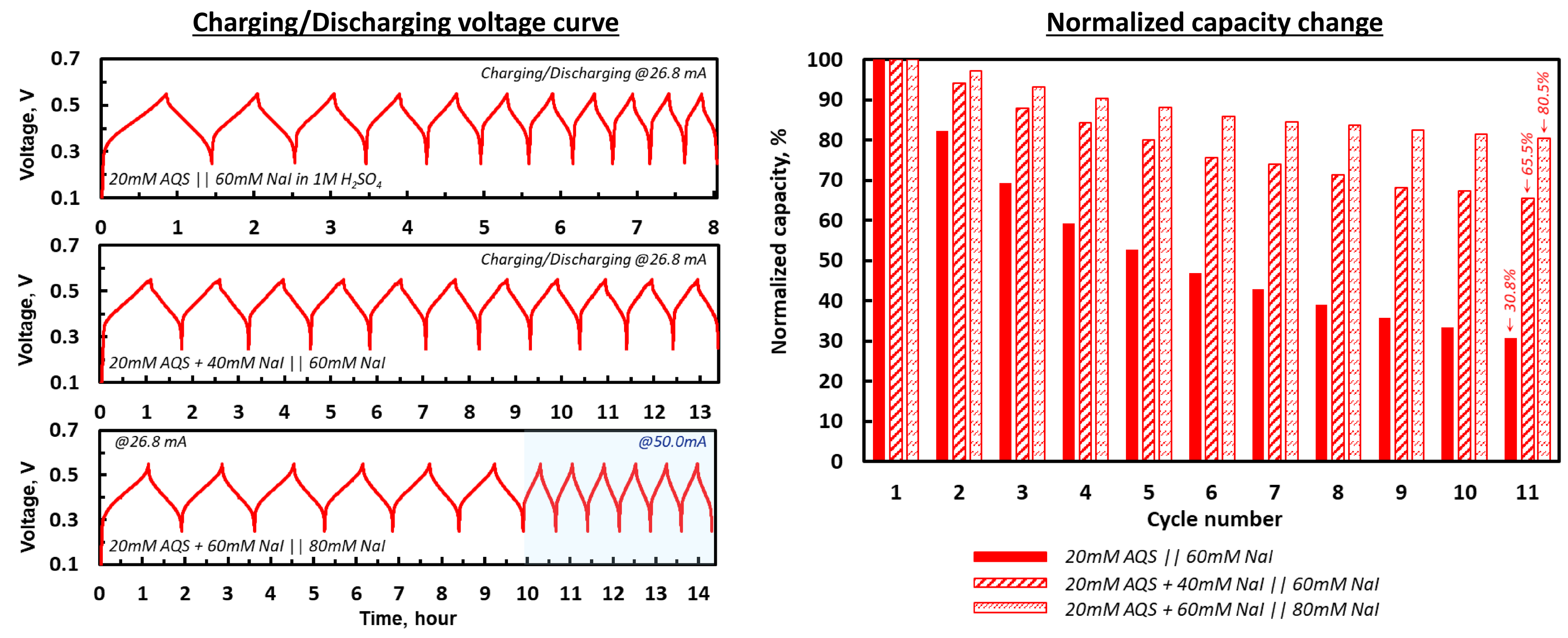
- Direct contact of the $Fe(CN)_6^{3-/4}$ catholyte with photon leads to degradation which results in coloration.
- Degradation (*e.g.*, Prussian blue formation) can be avoided by complete isolation of the electrolyte using a back-illumination approach. No significant photocurrent decrease has been observed.

Challenge #2 *Low cell voltage*





- p-GaP/n-TiO_2 heterojunction device showed un-biased photocharging of redox couples with $V_{cell} = 0.45$ V.



- Charging/Discharging (RFB) test reveals mixed catholyte (AQS+NaI) showed improved stability in capacity.

Conclusions

- ✓ A single TiO_2 protected c-Si based SRFB with $Fe(CN)_6^{3-/4-}$ and TEMPO has been demonstrated successfully.
- ✓ Degradation issue of the $Fe(CN)_6^{3-/4-}$ can be solved by the back-illumination approach. Complete isolation from the photon suppresses Prussian blue formation.
- ✓ p-GaP/n-TiO_2 showed unbiased charging of redox couples (AQSH and NaI) with V_{cell} over 0.45 V.

Project Outlook

- Back-side illumination using bifacial GaP device will be conducted to overcome poor photocurrent output.
- Studies on catalyst will be carried out for replacing Pt. Various conductive materials to suppress hydrogen evolution reaction will be tested (*e.g.*, carbon).
- Surface reaction monitoring (especially for AQS+NaI mixed electrolyte) carried out using SECM technique.

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Publication list