Final report – Stretchable all-organic rechargeable batteries

Results

Short summary

The project achieved the overall goal of developing a novel class of stretchable all-organic rechargeable batteries. This was achieved by the successful implementation of the four work packages:

- WP1 – Two typed of organic stretchable electrodes were developed, one dense composite electrode and one microporous foam electrode.
- WP2 – Two types of stretchable ion separators were developed, one stretchable hydrogel separator and one ion selective cellulose nanofibrils separator.
- WP3 – Stretchable batteries were assembled and characterized.
- WP4 – A demonstrator including a 4-cell battery and a LED was developed.

Two designs were developed for constructing the stretchable organic batteries:

- Approach 1 comprised dense composite electrodes and a hydrogel separator. Here the redox molecules were assembled directly on the conducting polymer electrodes.
- Approach 2 comprised microporous foam electrodes with soluble redox molecules and an ion selective separator. This potentially allows for a higher loading of redox molecules which reduce the cost of the device.

Approach 1 - dense composite electrodes.

The project started with the development of the redox-enhanced stretchable electrodes (WP1). After some initial trials a promising material composition was found based on an aqueous mixture of the conducting polymer PEDOT:PSS, the ionic liquid EMIM:TCM, the redox molecule alizarin sulfonate (ARS), and water dispersed polyurethane (Figure 1a). When deposited and dried, the composite shows a fibrillar structure (Figure 1b) and retains outstanding conductivity for ARS:(PEDOT:PSS) mass ratios (m_A/m_P) up to 3 (Figure 1c). The composite also shows outstanding stretchability (Figure 1d) and conductivity under strain (Figure 1e).

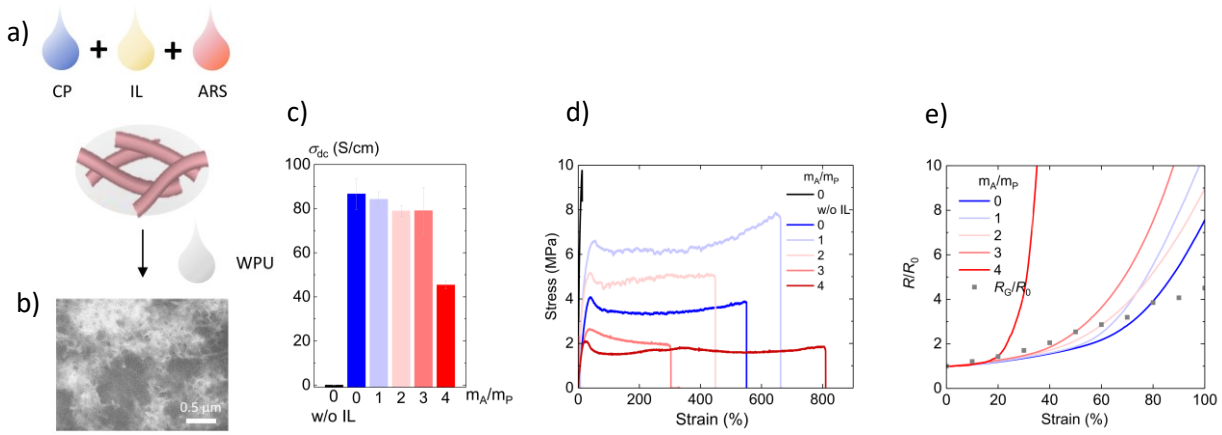

Figure 1*. a) An aqueous dispersion is formulated by mixing PEDOT:PSS (CP), ionic liquid (IL), alizarin sulfonate (ARS) and water dispersed polyurethane (WPU). b) The dried composite has a fibrillar morphology. c) The electrical conductivity is preserved for ARS:(PEDOT:PSS) ratios <= 3. d) The*

maximum strain is above 200 % for all samples. e) The electromechanical characteristics are good for ARS:(PEDOT:PSS) ratios <= 3.

Next, the charge storage capacity was evaluated for the various m_A/m_P ratios. It was found that the charge storage capacity increased with increasing amount of ARS (Figure 2). However, due to deteriorating electromechanical performance for m_A/m_P=4 (Figure 1e), m_A/m_P=3 was chosen as the optimal formulation to be evaluated further.

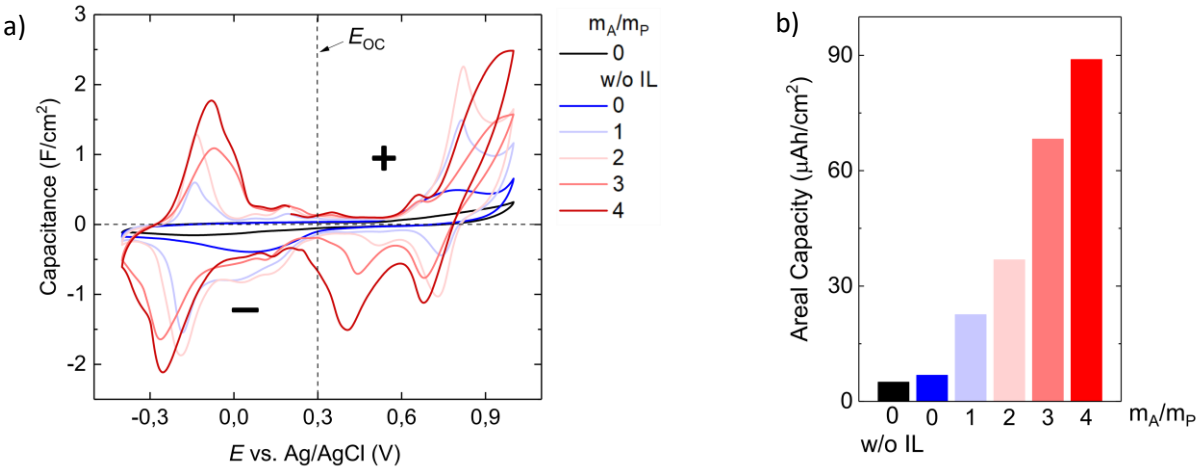

***Figure 2**. a) Cyclic voltammograms for the various electrode compositions. b) The areal charge storage capacity increase with the amount of added ARS.*

To assess the performance of the developed electrodes in a more realistic setting, a first prototype of a battery cell was developed by sandwiching two electrodes with a stretchable polyvinyl alcohol separator in between (Figure 2a). The performance of the cell was compared for two electrode types with m_A/m_P=0 and m_A/m_P=3 (Figure 3b-d). As can be seen from the characterization the addition of ARS improved the charge storage capacity dramatically with up to 20 times with respect to the pure conducting polymer electrodes.

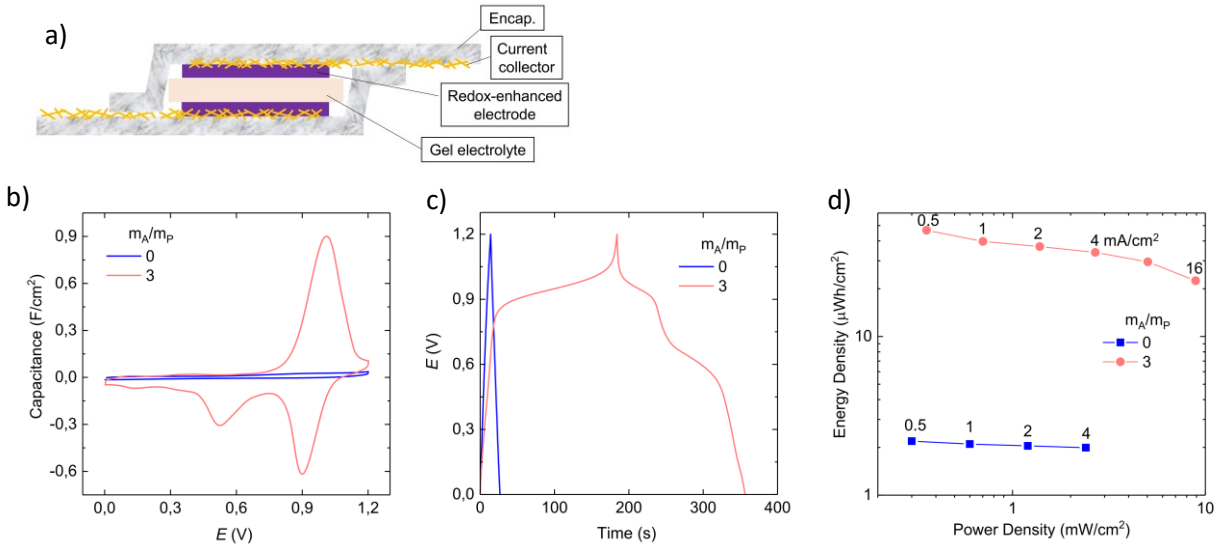

***Figure 3**. a) Schematic of a first version of the battery cell structure. b) Capacitance vs voltage for the battery. c) Galvanostatic charge-discharge of the battery. d) Ragone plot of the battery.*

Next, the performance of the developed battery cell was evaluated under mechanical strain. The performance was unchanged up to 80% strain (Figure 4), which is good news as these levels of strain are sufficient for all wearable applications. The battery survived strains up to 120% with only minor decrease in performance.

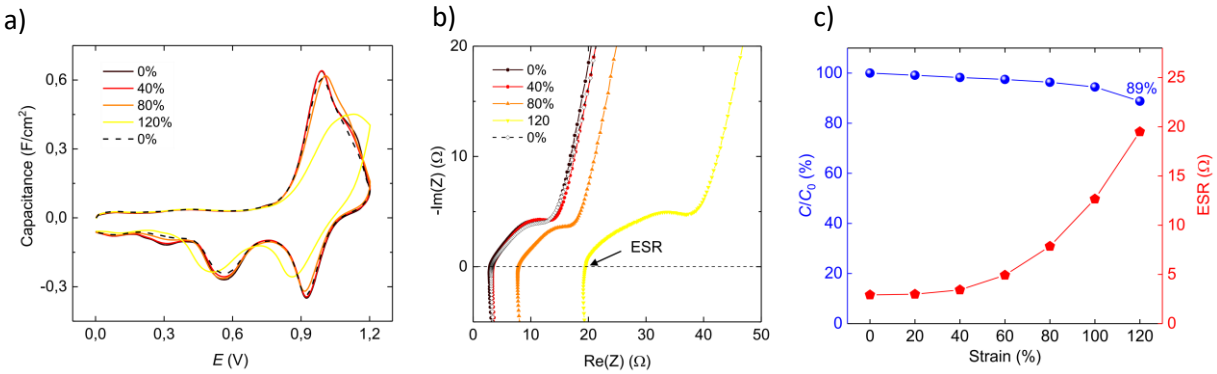

***Figure 4**. a) Capacitance vs mechanical strain for the battery. b) Impedance spectroscopy of the battery under strain. c) Normalized charge storage capacity (C/C_0) vs strain and internal resistance vs strain.*

Finally, a demonstrator was developed comprising four battery cells in series, a switch, and a mounted red LED. The integration of the demonstrator was successful and it could be repeatedly recharged and drive the LED while being stretched.

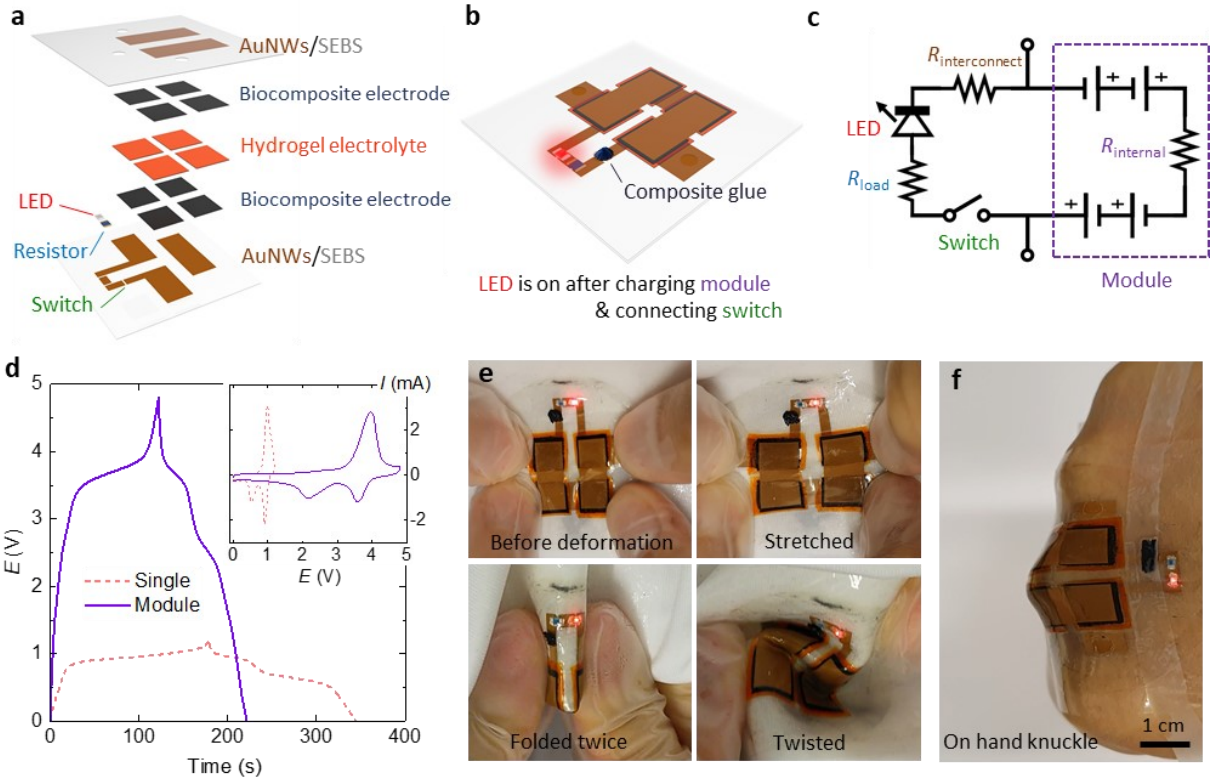

***Figure 5**. Wearable stretchable organic battery module. a) Exploded view of a stretchable circuit comprising a module with 4 cells connected in series, a resistor, a switch and a red LED. b) Schematic*

illustration of the complete module in operation. A piece of CP:IL:WPU composite was used as a conductive glue to close the switch. c) Equivalent circuit diagram of the stretchable circuit. Rload, Rinterconnect, and Rinternal denote resistances of a current limiting resistor, AuNW interconnects, and the internal resistance of a module, respectively. d) Comparison of GCD curves (CV curves in the inset) between a single device and a module. The current density is 1 mA cm-2 with respect to a single cell of the module. The CV scan rate is 10 mV s-1 for the single cell and 40 mV s-1 for the module. e) Photographs of the module attached to a stretchy fabric. The module remains functional (powers the LED) at various deformation conditions. f) Photographs of the module attached to a human hand wearing a transparent poly glove.

Approach 2 - microporous foam electrodes

This approach relied on porous electrodes with soluble organic redox molecules for energy storage. The advantage is that this decouples the necessary amount of more expensive electrode materials from the cheap redox molecules, thereby making the technology cheaper and more sustainable.

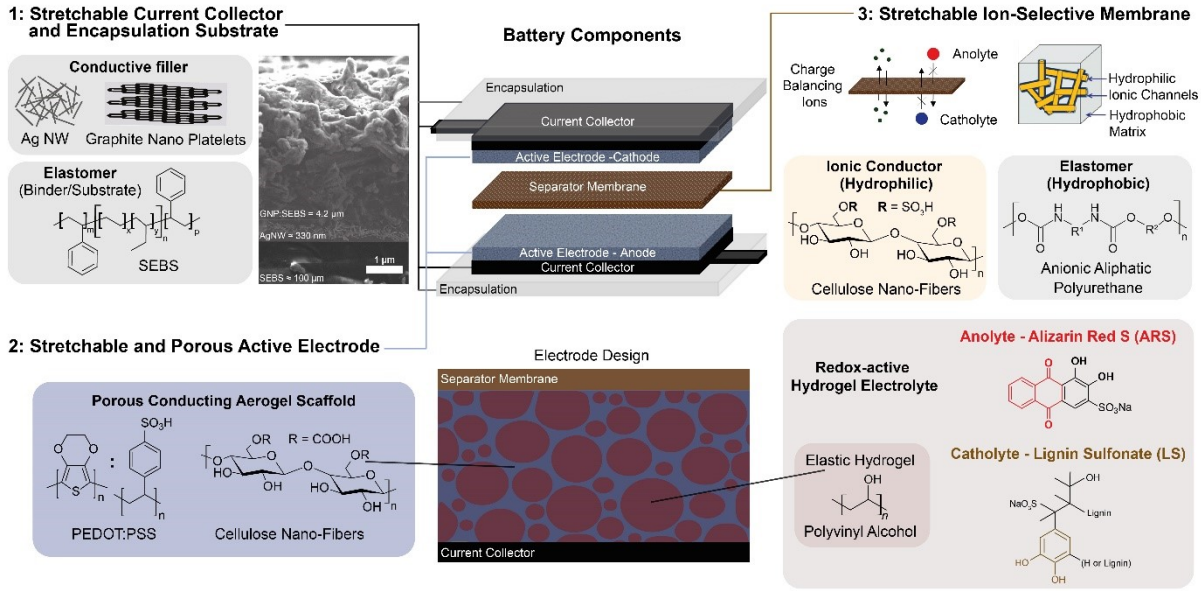

Figure 6. *Stretchable organic porous electrode battery. 1) The current collector comprises a stretchable graphite nano platelets composites with a ultra-thin layer of silver nanowires to improve conductivity. 2) The electrodes are made of porous cellulose nanofibril foam coated with PEDOT:PSS. 3) A stretchable ion selective separator was developed based on elastomer and cellulose nanofibrils.*

The porous electrodes were loaded with RS-containing hydrogels to improve the charge storage performance (Figure 7).

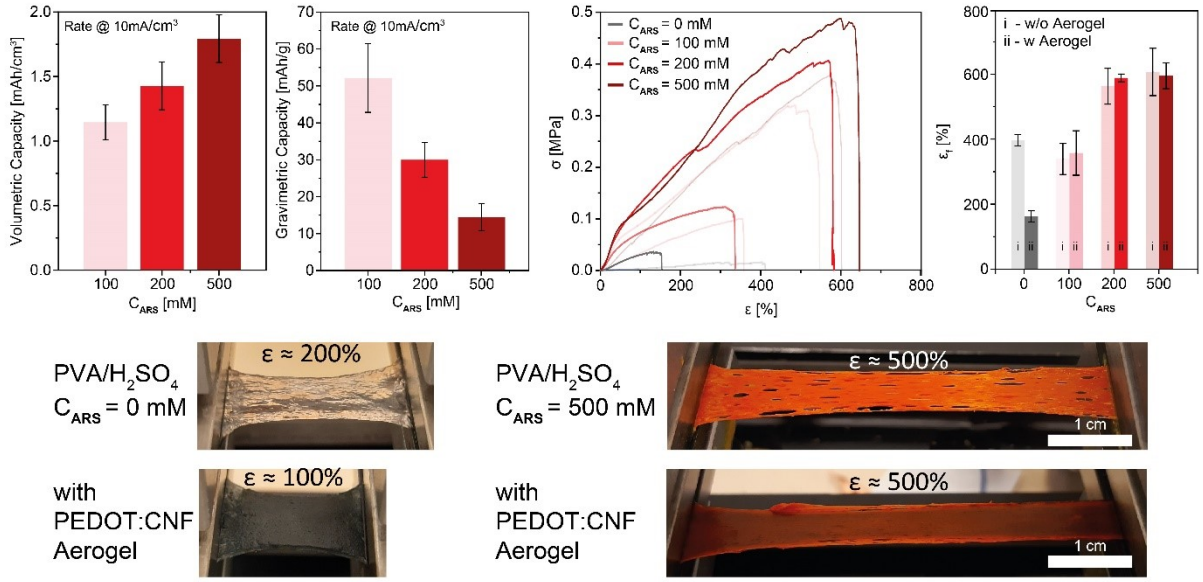

Figure 7. *Porous electrodes loaded with ARS. The volumetric capacity of the electrodes increased by the loading concentration of ARS, while the gravimetric capacity decreased, indicating that not all ARS were accessible at higher loading concentrations. The stretchability of the PVA-ARS hydrogels improved with ARS concentration. Interestingly, the amounts of defects in the gels decreased under strain when the porous electrode was incorporated (bottom right).*

When evaluating both anodes and cathodes of the batteries, we found that the cathodes based on ARS were less stable. We therefore replaced the ARS with another biomolecule, lignosulfonate (LS). This significantly improved the stability of the cathode during charge-discharge cycling (Figure 8).

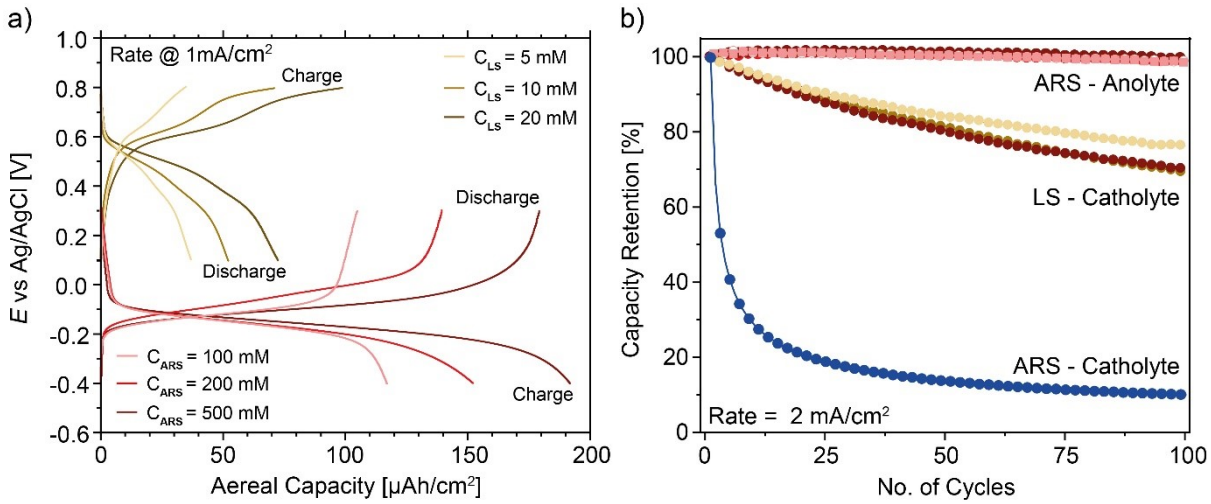

Figure 8. *Charge-discharge cycling of ARS and LS loaded electrodes. a) The low molecular ARS can be loaded at a much higher concentration than the polymeric LS, thereby providing higher charge storage capacity. b) The ARS anolyte showed good cycling stability while the ARS catholyte showed rapid degradation. LS catholyte showed much improved stability with respect to ARS.*

Summary
To summarize, stretchable all-organic electrodes of outstanding performance has been developed and tested in a battery cell configuration. These results are very promising and has generated new research efforts within this area. One manuscript is submitted on the approach 1 and two manuscripts are being prepared on approach 2.

Project implementation
The start of the project got delayed as one postdoc candidate dropped out in the last minute and then the COVID-19 pandemic happened. Because of this the project was granted a 5-month extension for the final report. A postdoc, Dr. Aiman Rahmanudin, was recruited and worked in the project on approach 1 (see above). Another postdoc, Dr. Nara Kim, also worked part time in the project and developed Approach 1. Overall, the project was implemented according to the time plan and all milestones were successfully reached.