Towards Increasing the Operating Potential Window of Aqueous Supercapacitors through the Passivation of Carbon-based Electrodes by Electrodeposition of Poly(phenylene oxide)

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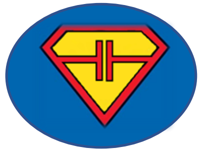
Abstract

The main drawback of supercapacitors when compared to batteries is their low energy density, which is mostly limited by the breakdown voltage of the electrolyte. Commercial devices typically use organic solvents, which can withstand up to 2.7 V, but are toxic and expensive. Aqueous electrolytes would be a cheaper and environmentally friendly alternative if their electrochemically stable potential window (ΔV≈1V) could be extended. A conceivable way to achieve this is by electrodepositing an insulating material on the surface of the carbon-based electrode. Poly(phenylene oxide) was identified as a suitable candidate. For a successful passivation, the deposited material must be thick enough to prevent electron transfer between the electrode and the electrolyte (>2 nm) whilst simultaneously thin enough (<30 nm) to preserve the electrode's high surface area, indispensable for a high capacitance. Preliminary results suggest a trade-off between capacitance and degree of passivation: a decrease in both oxidation and reduction leakage currents (measured at constant potentials and respectively associated to the oxygen and hydrogen evolution reactions) comes at the expense of a capacitance loss. This work will present results comparing differing polymer electrodeposition conditions and how these correlate both to the passivation of the electrode and to its performance metrics.

The story behind…

vs



- ✓ High energy density (up to 270 Wh/kg[1])
- X Low power density (< 680 W/kg[1])
- X Low cyclability (< 3 000 cycles[1])

- X Low energy density (< 10 Wh/kg[2]) → $E = \frac{1}{2} C \Delta V^2$
- ✓ High power density (up to 80 kW/kg[2])
- ✓ High cyclability (>1 million cycles[2])

Breakdown voltage of the **electrolyte**

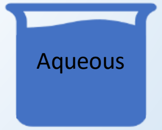
up to 3.5V

- ✓ Non-volatile[3]
- X Very expensive[3]
- X High resistivity[3]
- X Low accessibility to nanopores[3]
- ✓ Very large ΔV[3]

up to 2.7V

- X High volatility[3]
- X Expensive, toxic and flammable[3]
- X High resistivity[3]
- X Low accessibility to nanopores[3]
- ✓ Large ΔV[3]

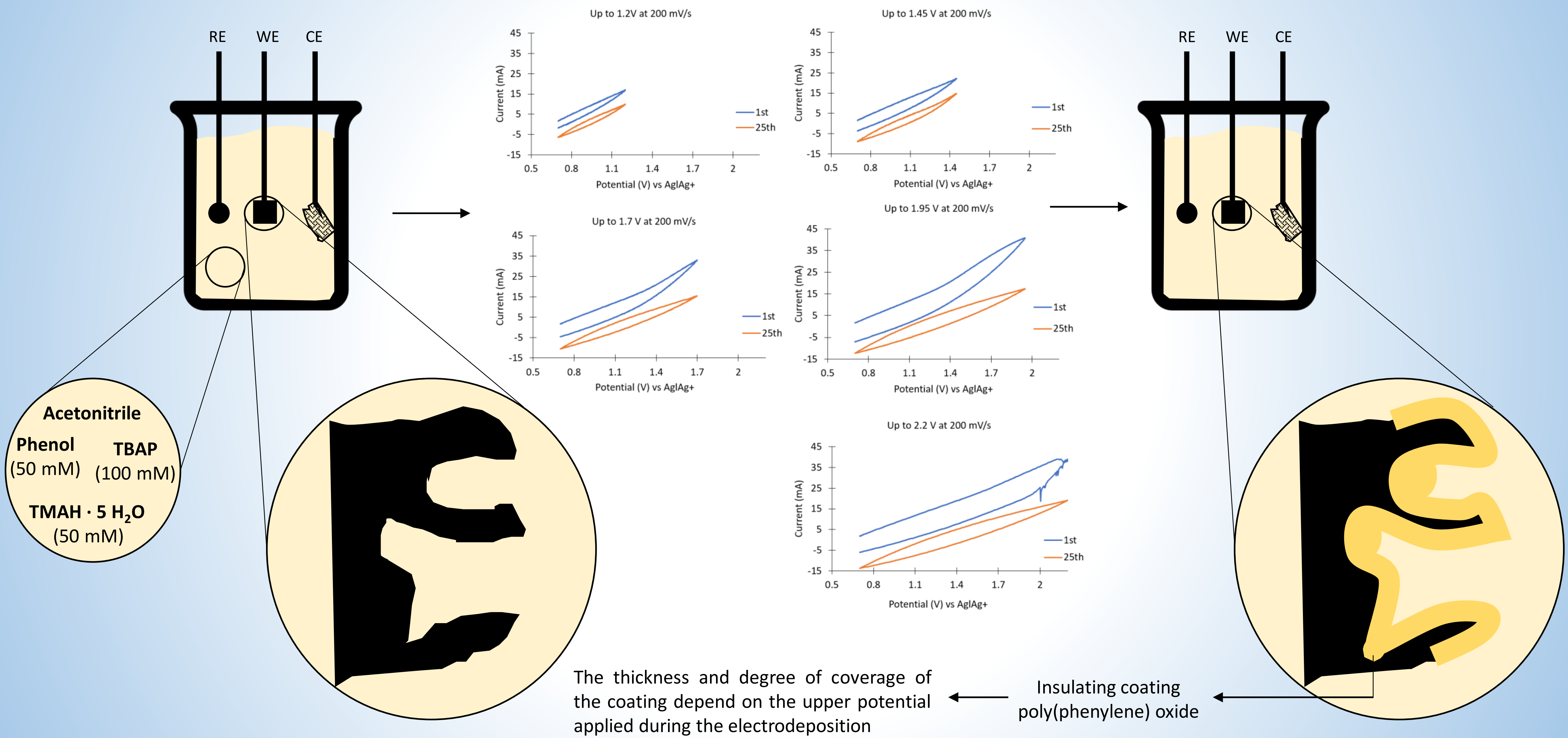
up to 1.2V



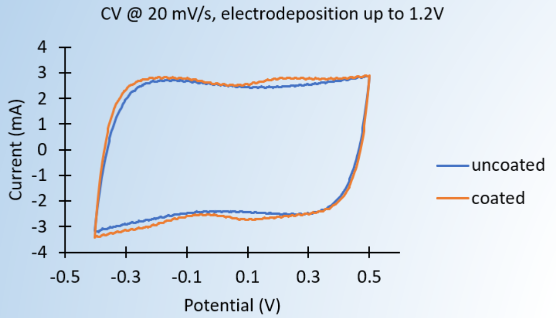
- ✓ Low volatility[3]
- ✓ Low cost and toxicity[3]
- ✓ Low resistivity[3]
- ✓ High accessibility to nanopores[3]
- X **Narrow ΔV**[3]

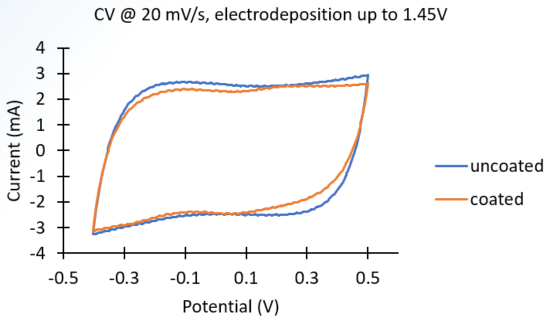
How to extend it??

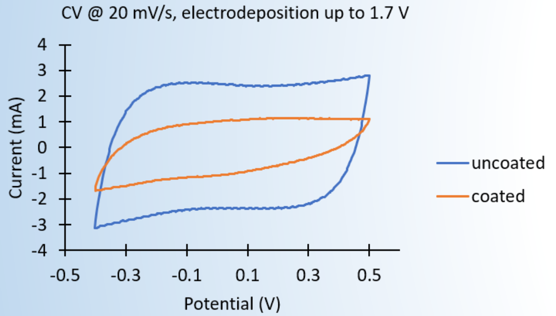
Passivation of Carbon-based Electrodes by Electrodeposition of Poly(phenylene oxide)

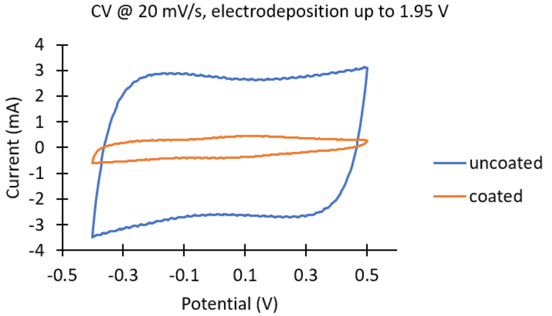


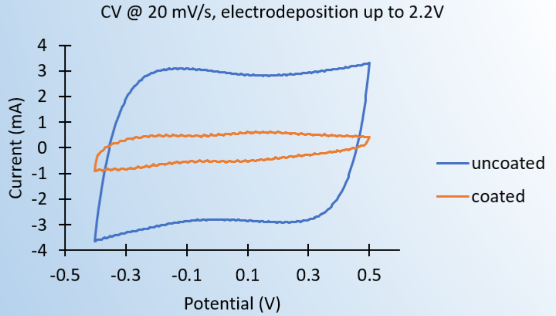
Impact of the coating on the capacitance

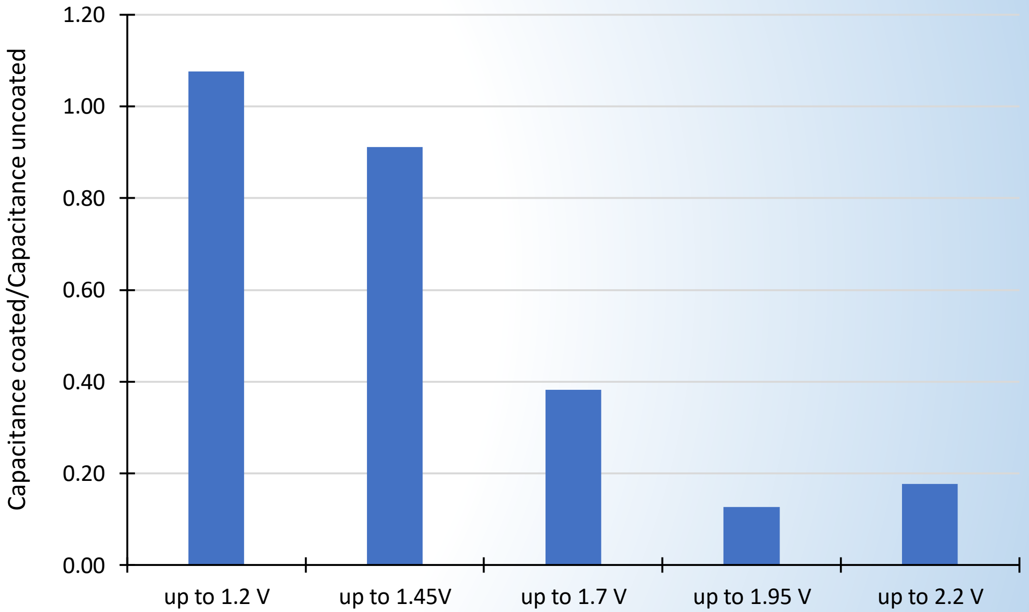




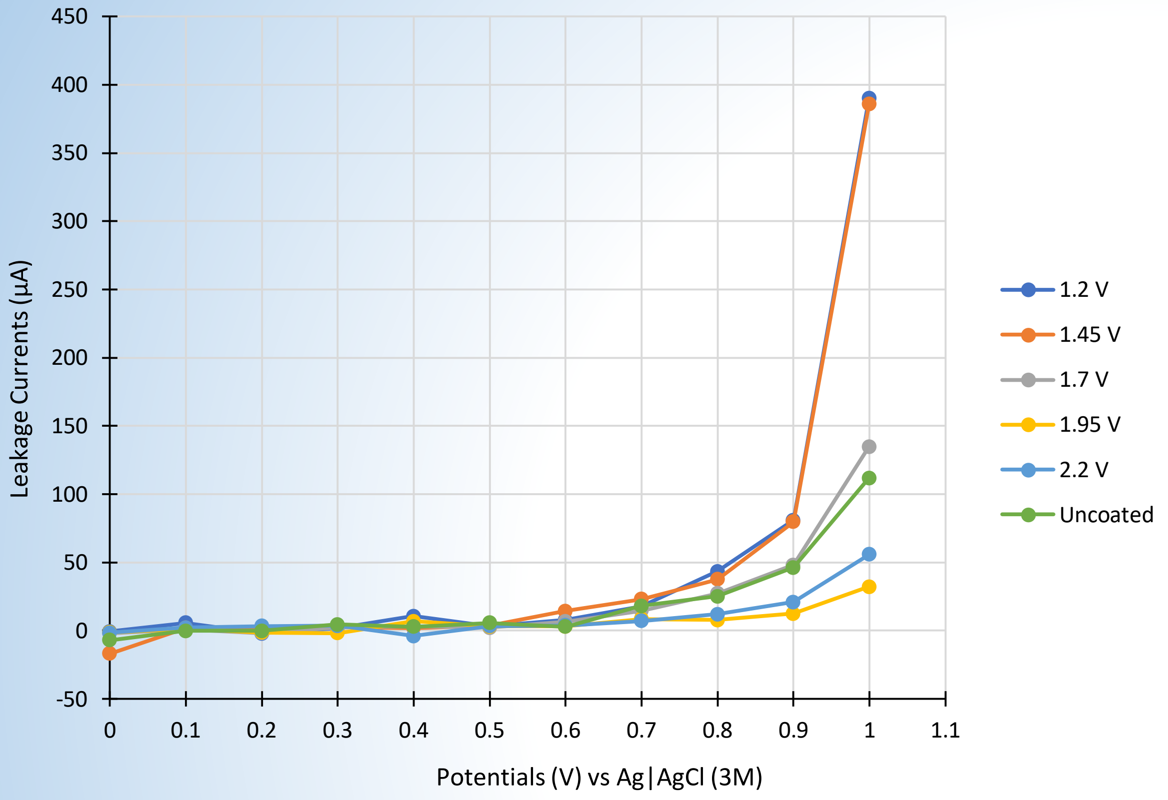








Effectiveness of the passivation



Preliminary conclusions and future work

- For upper potentials below 1.7V, the electrodeposited coating has a negligible impact on the capacitance
- Only for coatings electrodeposited up to potentials above 1.7V the coating seems to be effective in decreasing the leakage currents associated to water splitting
- For coatings electrodeposited up to potentials below 1.7V, the leakage current seems to be higher than the one obtained without any coating
- The effectiveness of the passivation should also be studied for the negative potential range
- The coatings should be electropolymerized up to potentials around 1.7V, and the features of the coating should be fine-tuned by varying the scan rate and the number of scans

References

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