Extending the voltage window of aqueous electrolytes for supercapacitors

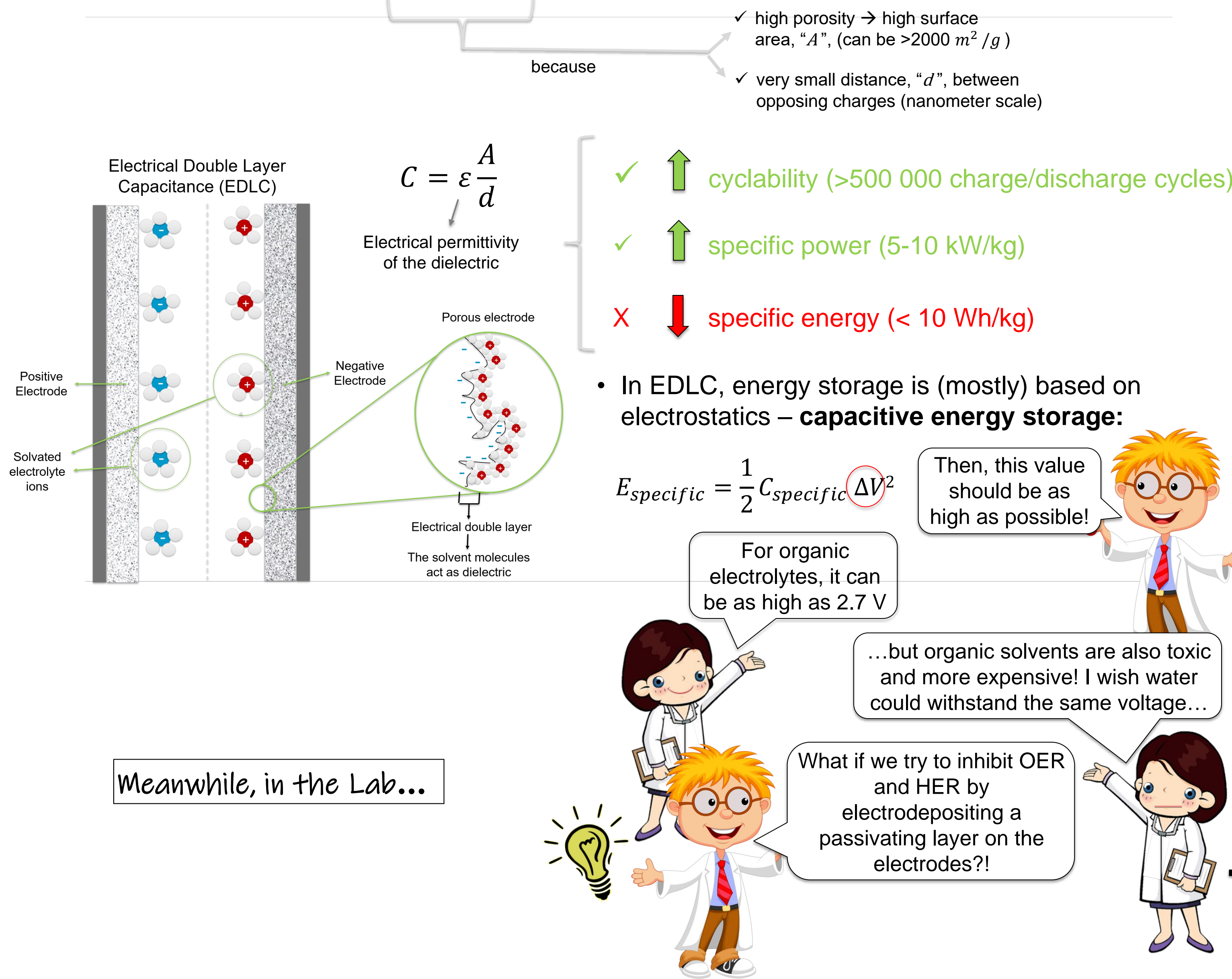Joana Monteiro Baptista[a,b], Jagdeep Sagu[b], Upul Wijayantha KG[b], Killian Lobato[a]

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Abstract

Currently, the main drawback of supercapacitors is their low energy density, which is mostly limited by the break-down 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, as long as its electrochemically stable potential window ($\Delta V \approx 1$ V) could be extended. A possible way to achieve this is by electrodepositing a passivating coating on the surface of the carbon-based electrode. For the passivation to be successful, it should be pinhole-free and thick enough to prevent electron transfer between the electrode and the electrolyte (>2 nm) while simultaneously thin enough (<30 nm) to preserve the electrode's high surface area, indispensable for a high capacitance. Polymer A has been identified as a suitable candidate for this insulating layer. This work aims at establishing the relationship between the thickness (and the coulombic efficiency) of the electropolymerized coating and the scan rate during the electrodeposition.

Supercapacitors

✓ high porosity → high surface area, "A", (can be >2000 m^2/g)
because
✓ very small distance, "d", between opposing charges (nanometer scale)

Electrical Double Layer Capacitance (EDLC)

$$C = \varepsilon \frac{A}{d}$$

Electrical permittivity of the dielectric

Positive Electrode — Negative Electrode
Solvated electrolyte ions
Porous electrode
Electrical double layer
The solvent molecules act as dielectric

✓ ⬆ cyclability (>500 000 charge/discharge cycles)

✓ ⬆ specific power (5-10 kW/kg)

X ⬇ specific energy (< 10 Wh/kg)

- In EDLC, energy storage is (mostly) based on electrostatics – **capacitive energy storage:**

$$E_{specific} = \frac{1}{2} C_{specific} \Delta V^2$$

Then, this value should be as high as possible!

For organic electrolytes, it can be as high as 2.7 V

…but organic solvents are also toxic and more expensive! I wish water could withstand the same voltage…

What if we try to inhibit OER and HER by electrodepositing a passivating layer on the electrodes?!

Meanwhile, in the Lab…

The passivating layer

Requirements:

- High dielectric constant, so that a thin layer (<30 nm) is enough to prevent the electron transfer between the electrode and the electrolyte)

- Insoluble in water (regardless of the pH)

- Electropolymerizable

- Uniform and pinhole-free

Polymer A seems to meet these criteria…

…However, the success of the passivation, also depends on the circumstances of the electropolymerization!
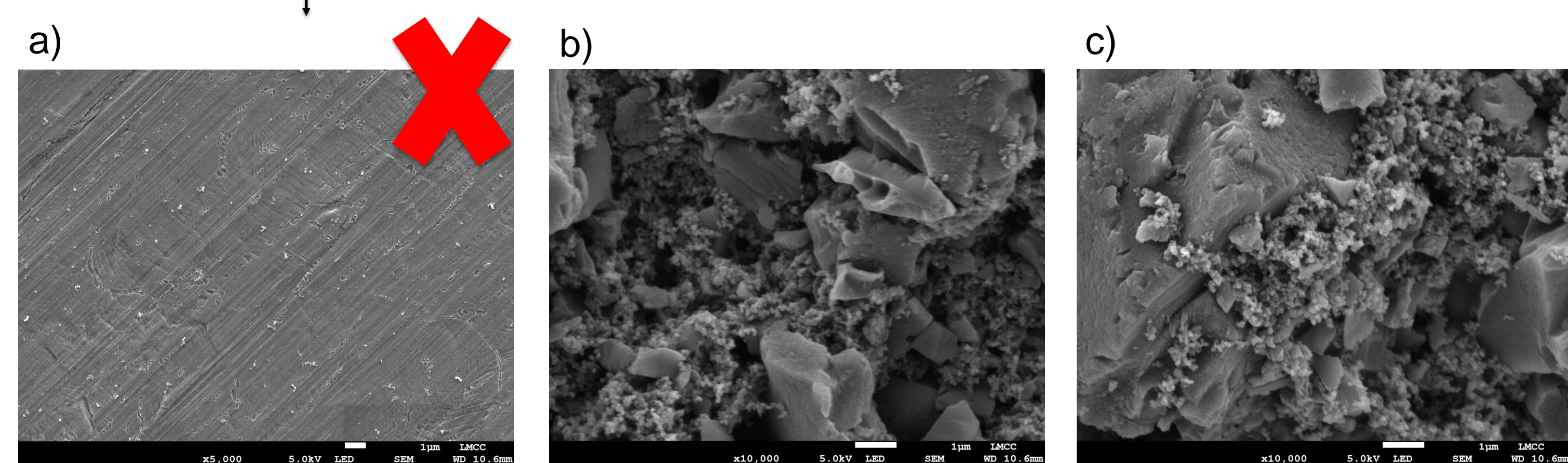

a) b) c)

Figure 1a) – Several pinholes are observable on the passivating layer electrodeposited on stainless steel; b) Activated Carbon (AC) electrode before the electropolymerization; c) AC electrode after the electropolymerization. No significant changes observable between b) and c). In a) and c), the electropolymerization was made by cyclic voltammetry **@ 20 mV/s.**

Perhaps too fast? Let's slow down a "little bit"…

Cyclic Voltammetry (@20 mV/s) of activated carbon electrode before and after the electropolymerization

Current (mA) vs Potential (V) against Ag/AgCl reference electrode
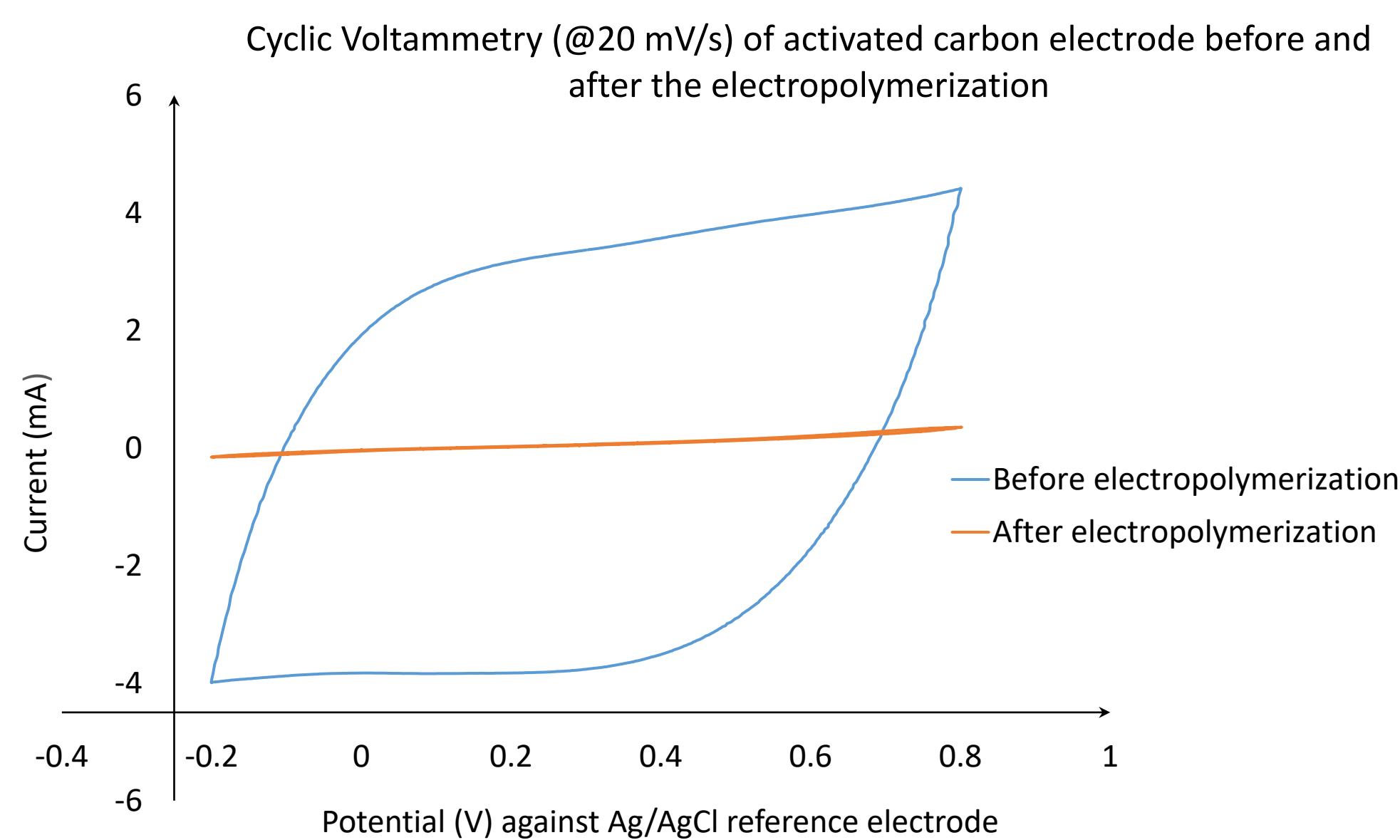— Before electropolymerization
— After electropolymerization

Figure 3 – Cyclic voltammetry @20 mV/s of the coated and the uncoated activated carbon electrode in an aqueous solution. **Good news:** an insulating layer was definitely deposited on the electrode. **Bad news:** this layer seems to have blocked the surface pores, hence dramatically reducing the capacitance.

Let's now compare the performance of the coated and the non-coated electrodes in a an aqueous electrolyte…

Electropolymerization (@0.5 mV/s) of Polymer A on activated carbon electrode

Current (mA) vs Potential (V) against Ag/AgCl reference electrode
— 1st cycle
— 2nd cycle
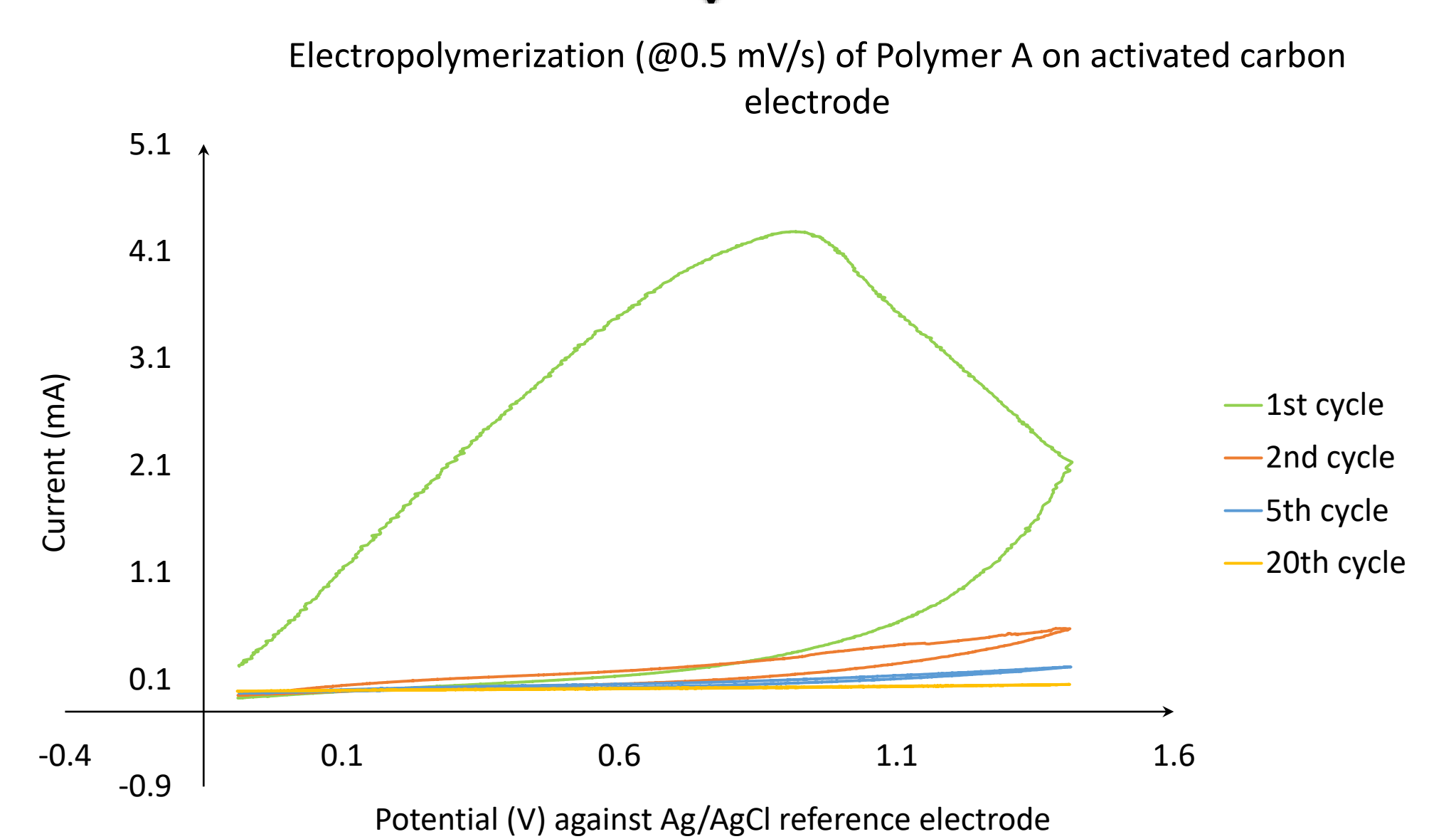— 5th cycle
— 20th cycle

Figure 2- Electropolymerization @ 0.5 mV/s of Polymer A on an AC electrode (70%AC, 20% binder, 10% conducting additive). Solution containing the monomer A: 50 mM of monomer A + 60 mM of NaOH in methanol. At the end of the self-limiting process, the current is negligible.

Where did all the capacitance go? 0.5 mV/s is way too slow! I really have to find the optimal scan rate for the electropolymerization…

You can try the electropolymerization at a range of scan rates, and see how it influences the film thickness (FT) and the coulombic efficiency (CE)!

$$CE = \frac{Q_{discharge}}{Q_{charge}} \times 100$$

$$FT = \frac{Q\ M}{A\ \rho\ F\ z}$$

- Q ⟶ charge transferred to the polymer
- M ⟶ molar mass of Polymer A
- A ⟶ estimated surface area of the carbon electrode
- ρ ⟶ density of Polymer A
- F ⟶ Faraday constant (96485.33 C/mol)
- z ⟶ number of electrons transferred per monomer

Film thickness and Coulombic efficiency vs scan rate

CE (%) / FT (nm) vs scan rate (V/s)
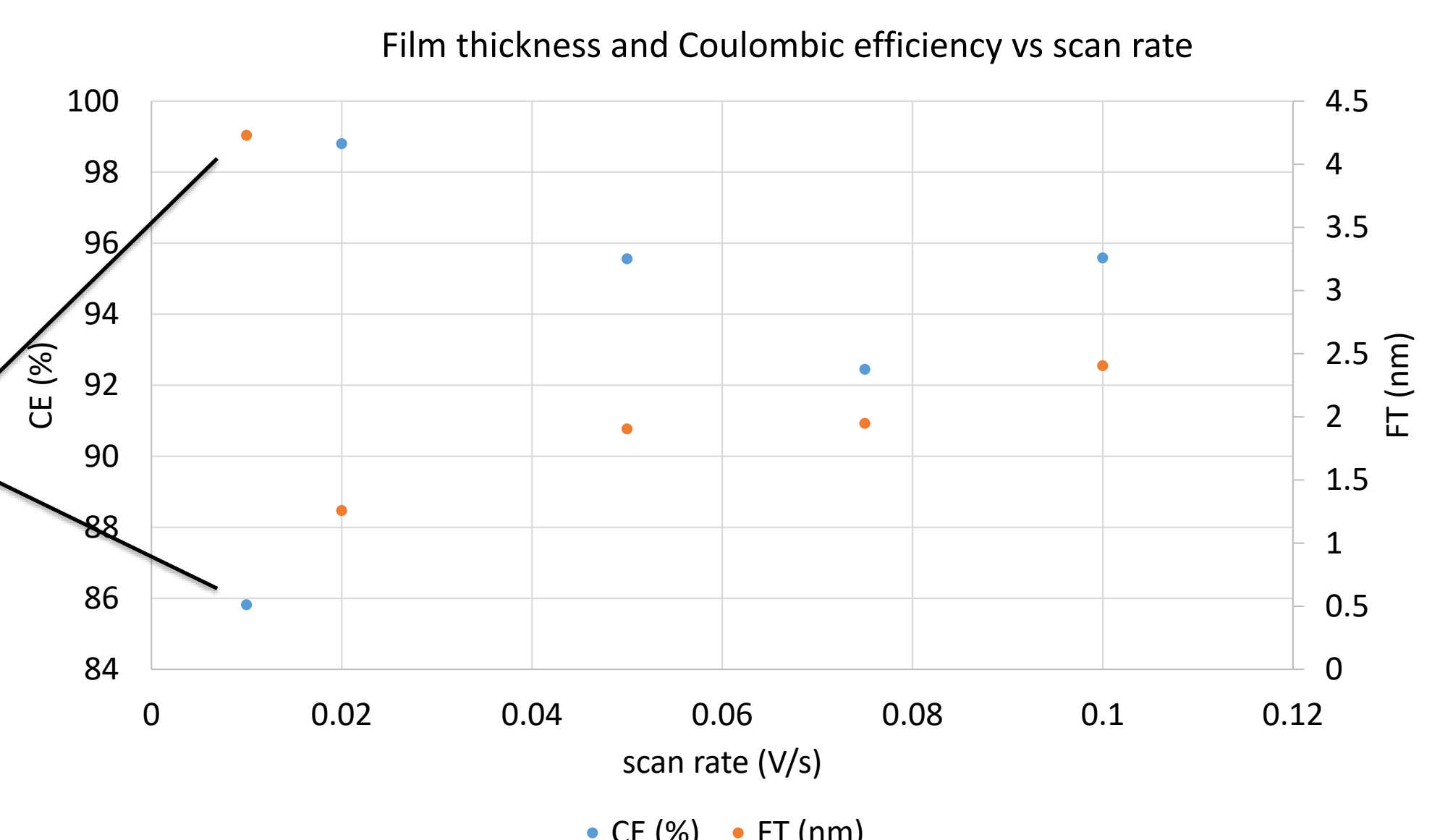• CE (%) • FT (nm)

Figure 4 – Coulombic efficiency and film thickness vs electropolymerization scan rate

Discussion

The thickness of the electrodeposited film seems to decrease dramatically as the scan rate of the electropolymerization increases from 10 mV/s to 20 mV/s. Then, at higher scan rates, it surprisingly seems to rise. Even more surprising is the fact that coulombic efficiency and thickness seem to be inversely related: apparently, the lower the thickness, the higher the coulombic efficiency. Indeed, the opposite behaviour was expected, since the coulombic efficiency is hindered by OER and HER (parasitic reactions) and, in principle, a thicker layer would enable a more effective passivation. A possible explanation for these observations is the existence of another parasitic reaction that also affects the coulombic efficiency. The authors hypothesize that, in thicker layers, there is a higher entrapment of unreacted monomers which can later suffer electropolymerization during the charge-discharge tests, hence decreasing the coulombic efficiency. In future experiments, the electrodes should be more thoroughly washed after the electropolymerization to minimize this effect. Also, the voltage window used in the charge-discharge tests will be extended, to promote OER and HER so that their impact on the coulombic efficiency is more pronounced than the impact of any other parasitic reactions. As such, the inhibition of water electrolysis by the passivating layer should then have a larger effect on the coulombic efficiency.