Towards increasing the stable potential window of aqueous supercapacitors through the passivation of carbon-based electrodes

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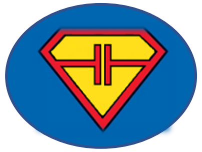
Symposium B – Battery and energy storage devices: from materials to eco-design

Introduction

vs



✗ Low cyclability (< 3 000 cycles [1])	✓ High cyclability (up to 1 million cycles [2])
✗ Low power density (< 680 W/kg [1])	✓ High power density (up to 80 kW/kg) [2]
✓ High energy density (up to 270 Wh/kg [1])	✗ Low energy density, E' (< 6.8 Wh/kg) [2]
↓	↓
Low €/Wh	High €/Wh

[1] K. Liu *et al.*, "A brief review on key technologies in the battery management system of electric vehicles," *Front. Mech. Eng.*, vol. 14, no. 1, pp. 47–64, 2019.
[2] SkeletonTechnologies, "SkelCap Industrial Ultracapacitor Cells," 2020. [Online]. Available: https://www.skeletontech.com/skelcap-sca-ultracapacitor-cells. [A

Introduction

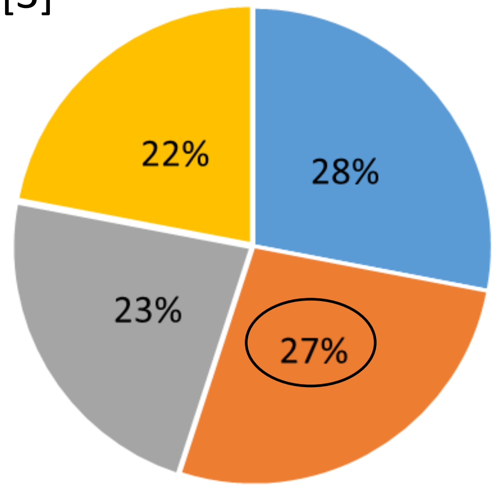
To decrease €/Wh....

Reduce costs

and/or

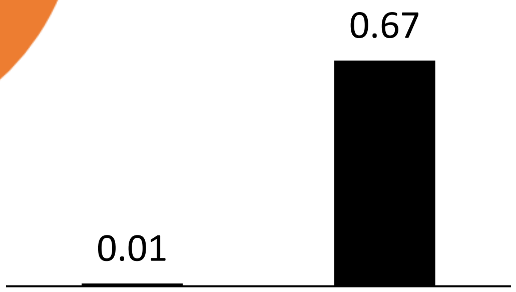
Increase energy density (E')

[3]



- Electrode materials
- Electrolyte
- Separator
- Cell parts and production

Cost (€/mL)

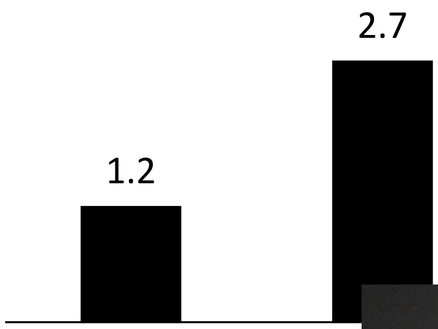


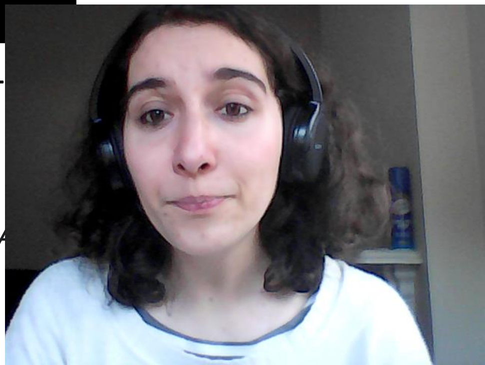
$$E' = \frac{1}{2} C' \Delta V^2$$

C' → specific capacitance

ΔV → stable voltage range

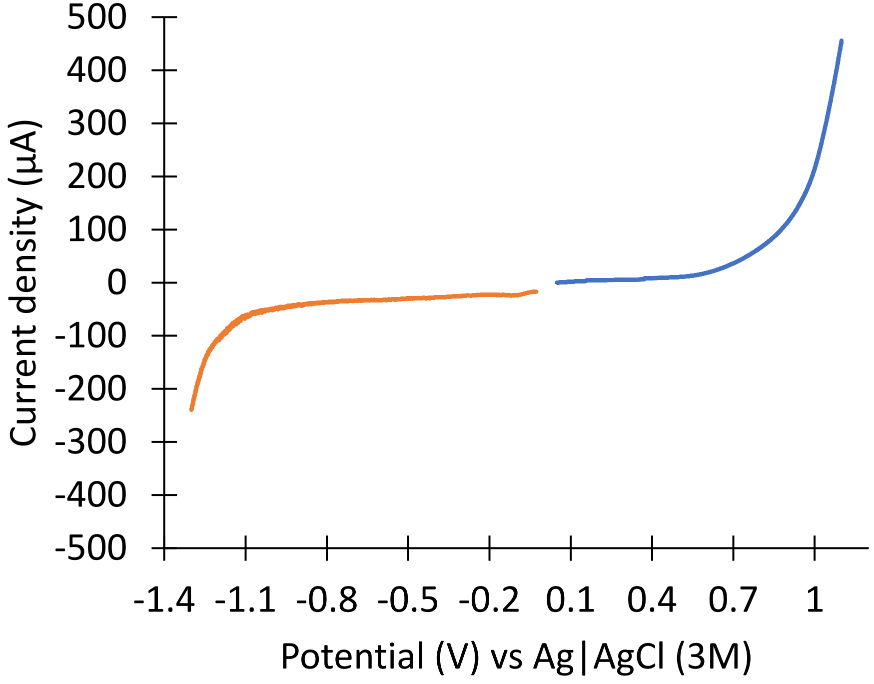
Operational ΔV





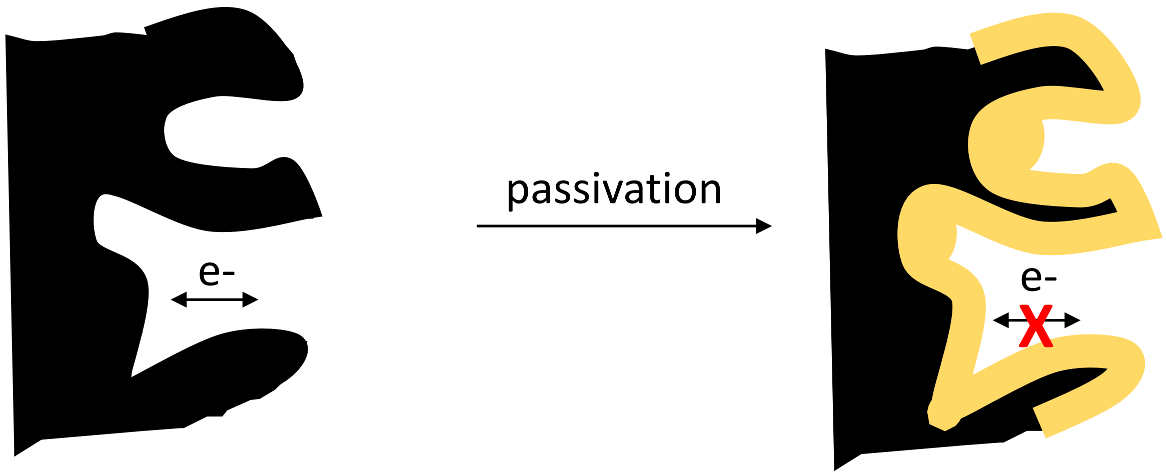
[3] Schütter et al., Industrial Requirements of Materials for Electrical Double Layer Capacitors: Impact on Current and Future Applications. A
1900334. https://doi.org/10.1002/aenm.201900334

Introduction

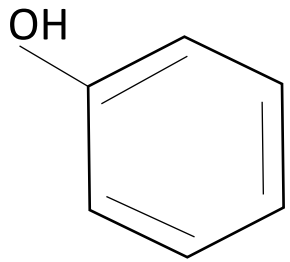


- Anodic and cathodic reactions leading to gas evolution
- The bubbles hinder the mechanical stability of the electrode and its electrical contact with the current collector
- Thus, as the cycles progress, the capacitance decreases and the resistance increases

Introduction



Polyphenylene oxide (PPO) meets these criteria!

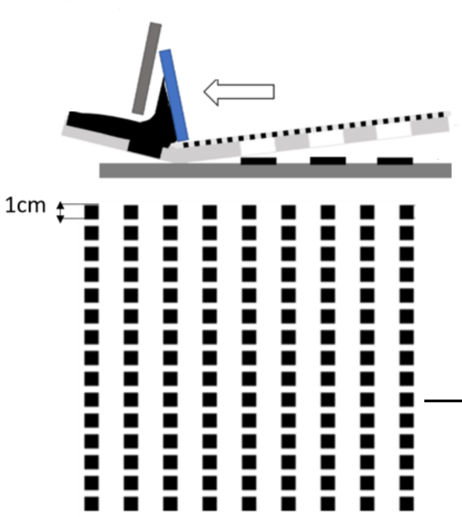


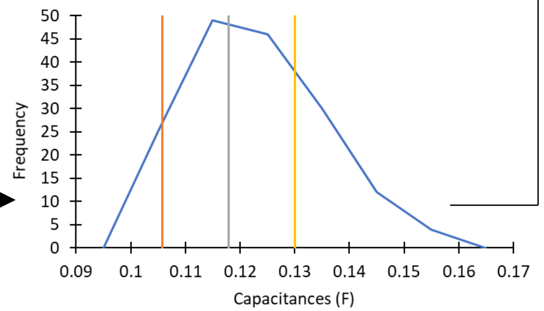
- ✓ Highly insulating
- ✓ Insoluble in the electrolyte
- ✓ Chemically and mechanically stable
- ✓ Thin (ca. 4 nm) → self-suppressed growth: thickness depends on resistivity

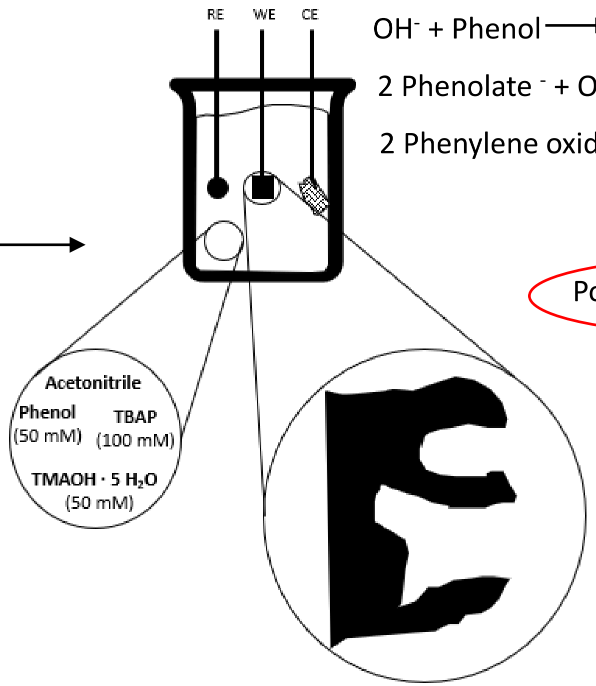
↓

effectiveness of passivation
vs
capacitance

Methodology







$OH^- + \text{Phenol} \longrightarrow \text{Phenolate}^- + H_2O$

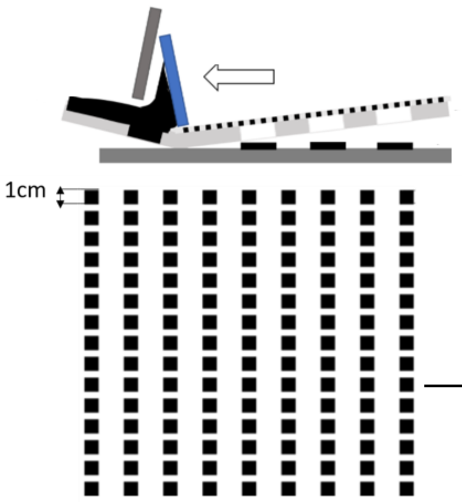
$2\ \text{Phenolate}^- + OH^- - 2e^- \longrightarrow \text{Phenylene oxide dimer}^- + H_2O$

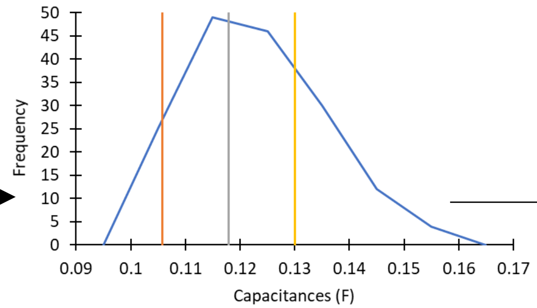
$2\ \text{Phenylene oxide dimer}^- + OH^- - 2e^- \longrightarrow \text{Phenylene oxide tetramer}^- + H_2O$

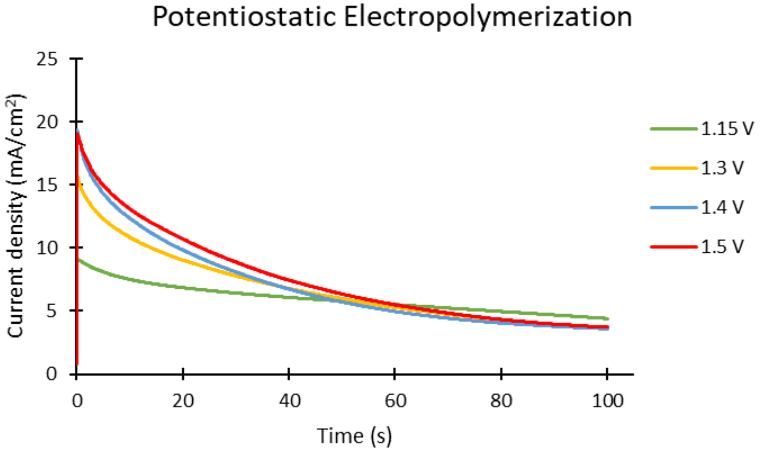
.
.
.

Poly(phenylene oxide)

Methodology



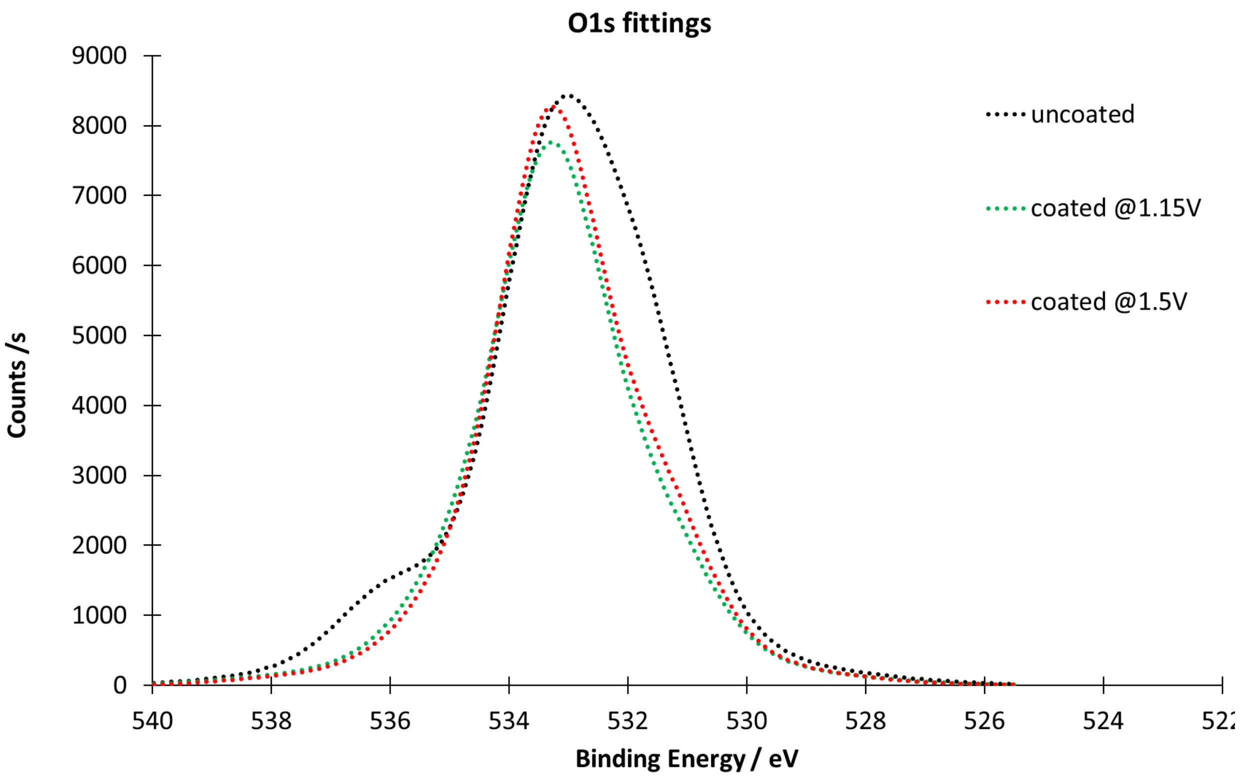




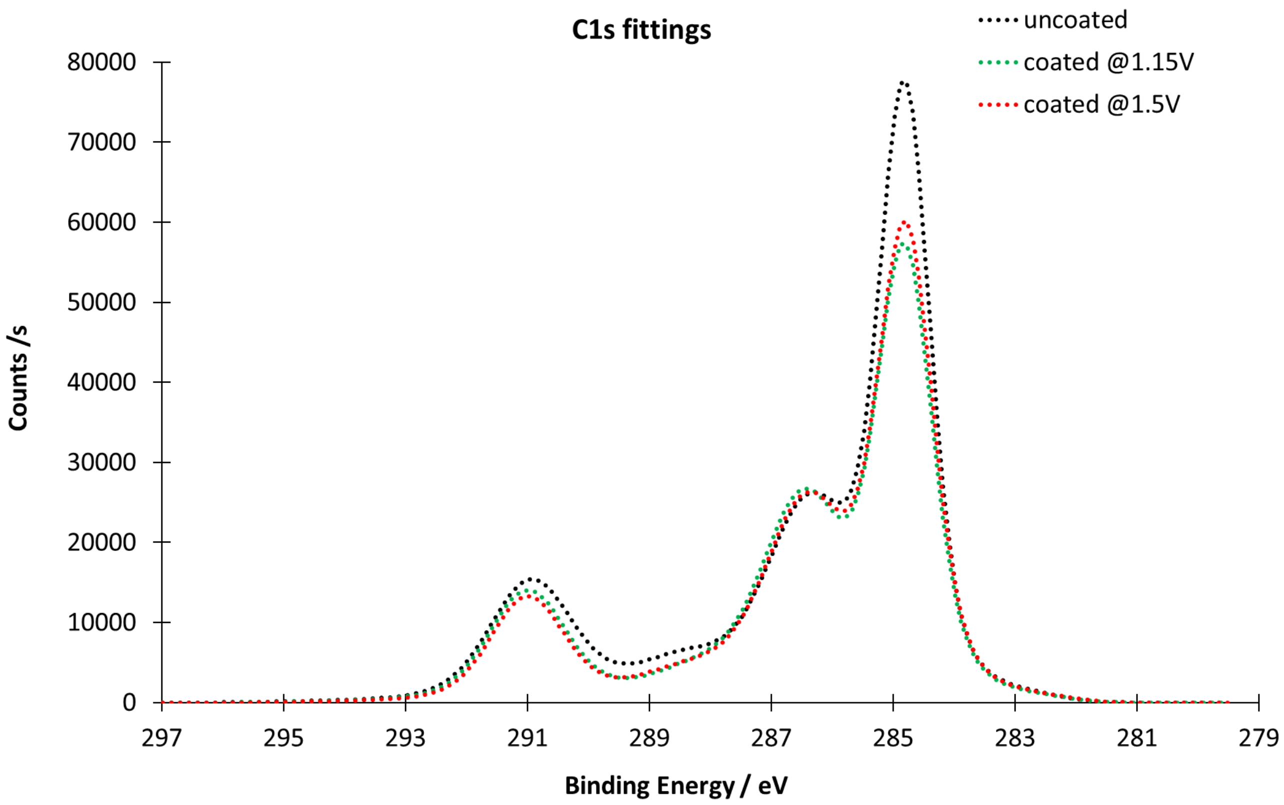
uncoated

- XPS
- CVs
- GCDs
- EIS
- Coin cells

Results
XPS



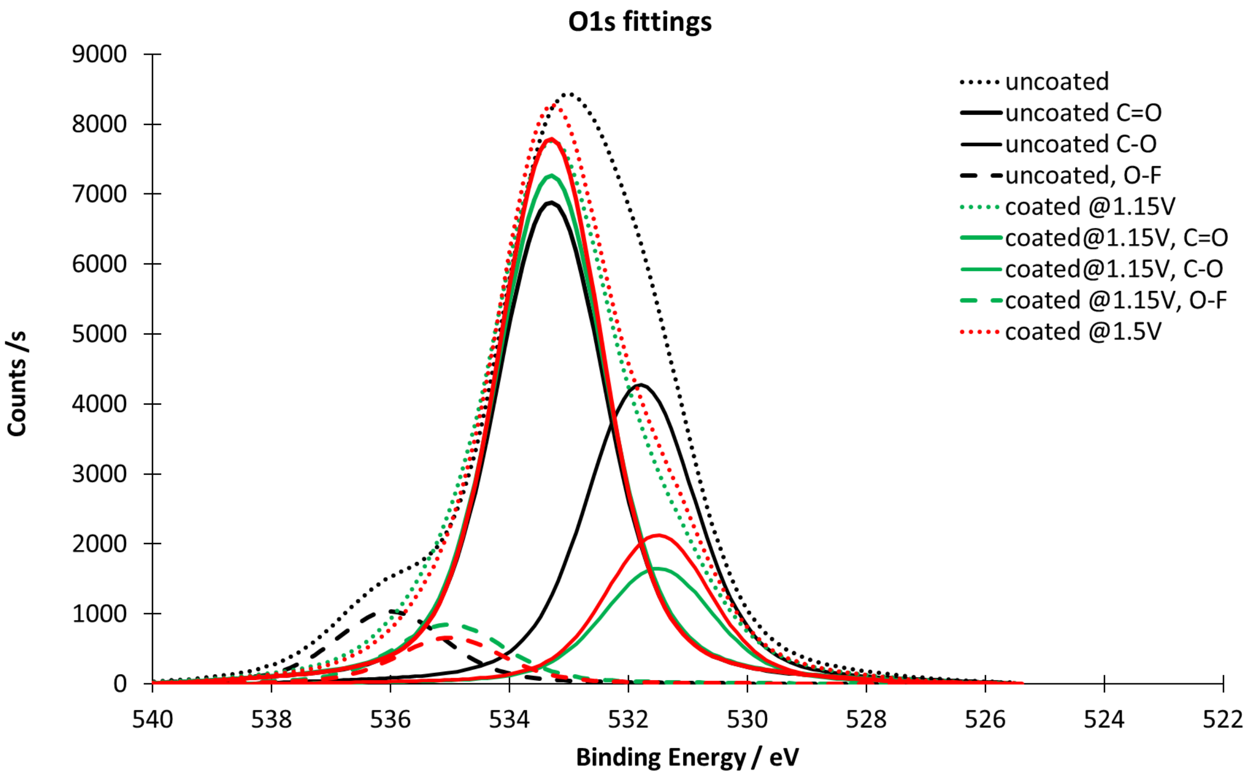
O1s fittings
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Counts /s
540
538
536
534
532
530
528
526
524
Binding Energy / eV
uncoated
coated @1.15V
coated @1.5V



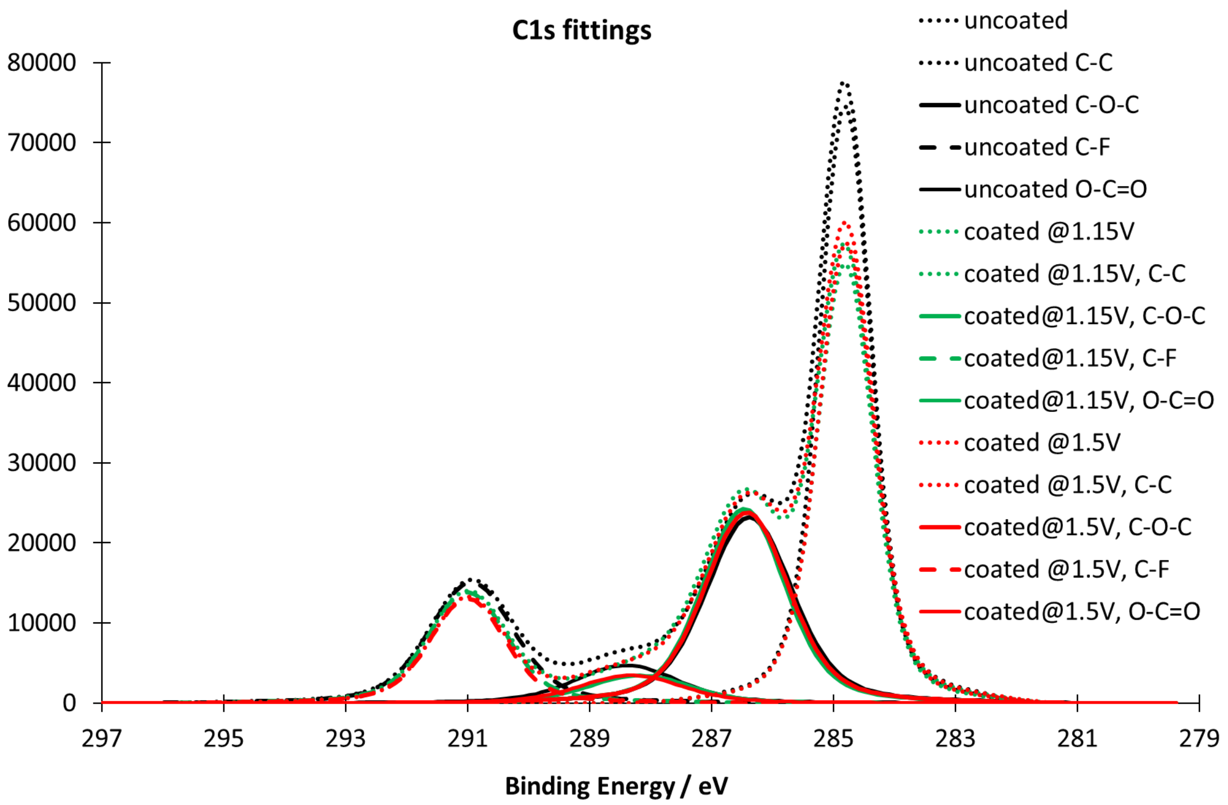
C1s fittings
80000
70000
60000
50000
40000
30000
20000
10000
0
Counts /s
297
295
293
291
289
287
285
283
281
279
Binding Energy / eV
uncoated
coated @1.15V
coated @1.5V

Results

XPS



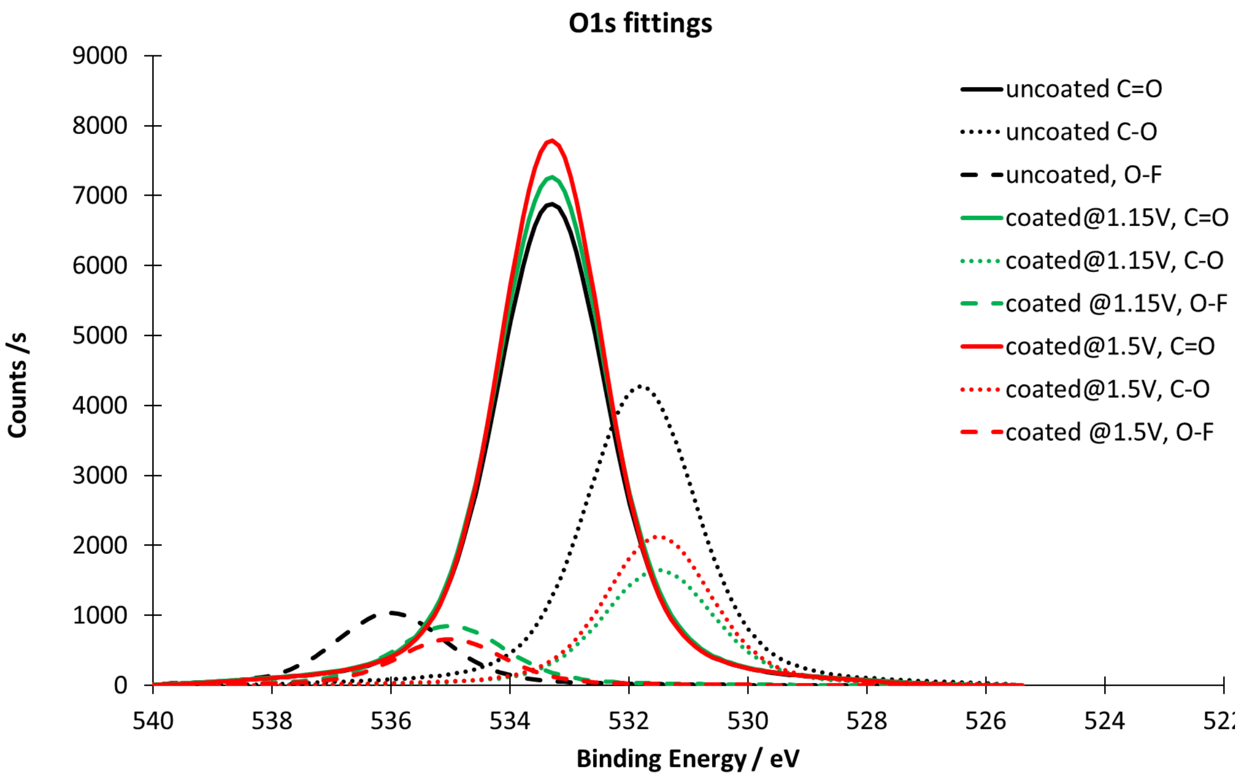
O1s fittings
Counts /s
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
540
538
536
534
532
530
528
526
524
522
Binding Energy / eV
uncoated
uncoated C=O
uncoated C-O
uncoated, O-F
coated @1.15V
coated@1.15V, C=O
coated@1.15V, C-O
coated @1.15V, O-F
coated @1.5V

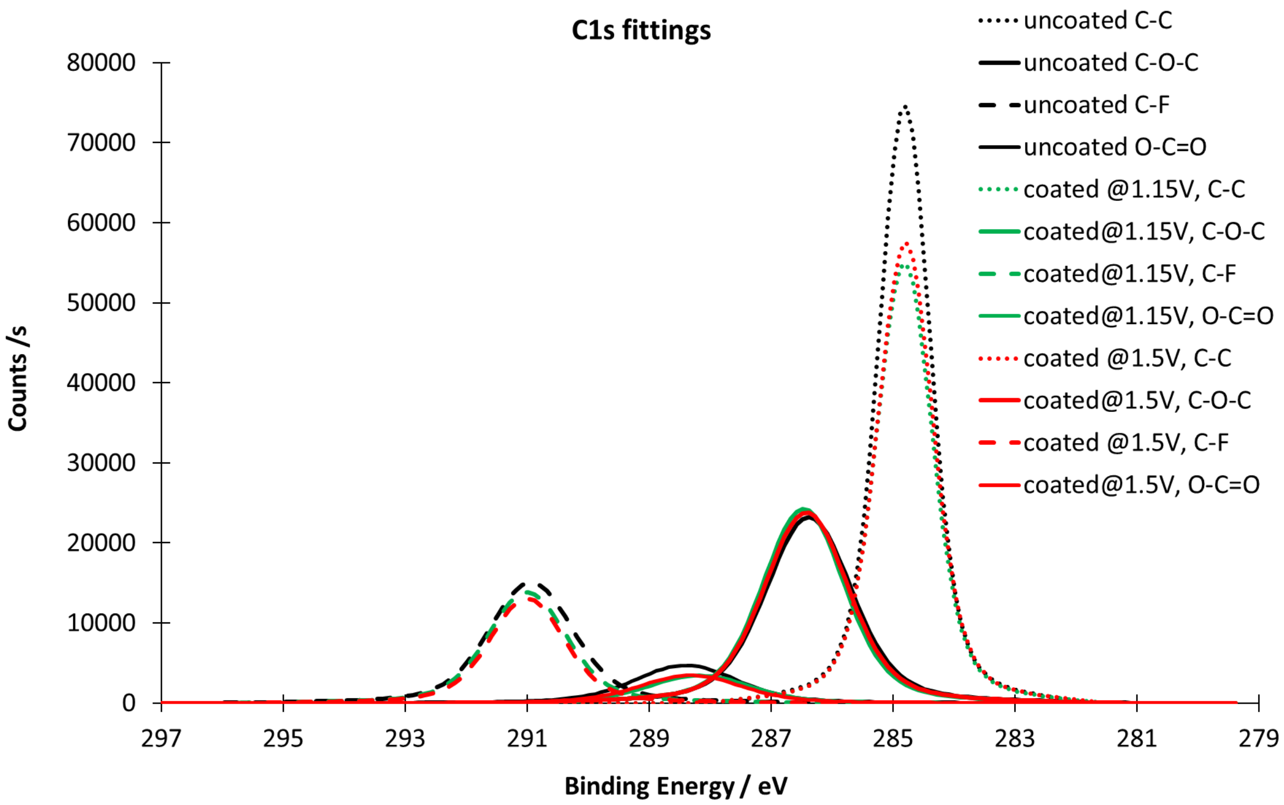


C1s fittings
80000
70000
60000
50000
40000
30000
20000
10000
0
297
295
293
291
289
287
285
283
281
279
Binding Energy / eV
uncoated
uncoated C-C
uncoated C-O-C
uncoated C-F
uncoated O-C=O
coated @1.15V
coated @1.15V, C-C
coated@1.15V, C-O-C
coated@1.15V, C-F
coated@1.15V, O-C=O
coated @1.5V
coated @1.5V, C-C
coated@1.5V, C-O-C
coated @1.5V, C-F
coated@1.5V, O-C=O

Results

XPS


O1s fittings
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Counts /s
540
538
536
534
532
530
528
526
524
522
Binding Energy / eV
uncoated C=O
uncoated C-O
uncoated, O-F
coated@1.15V, C=O
coated@1.15V, C-O
coated @1.15V, O-F
coated@1.5V, C=O
coated@1.5V, C-O
coated @1.5V, O-F


C1s fittings
80000
70000
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uncoated C-C
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uncoated O-C=O
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coated@1.15V, C-O-C
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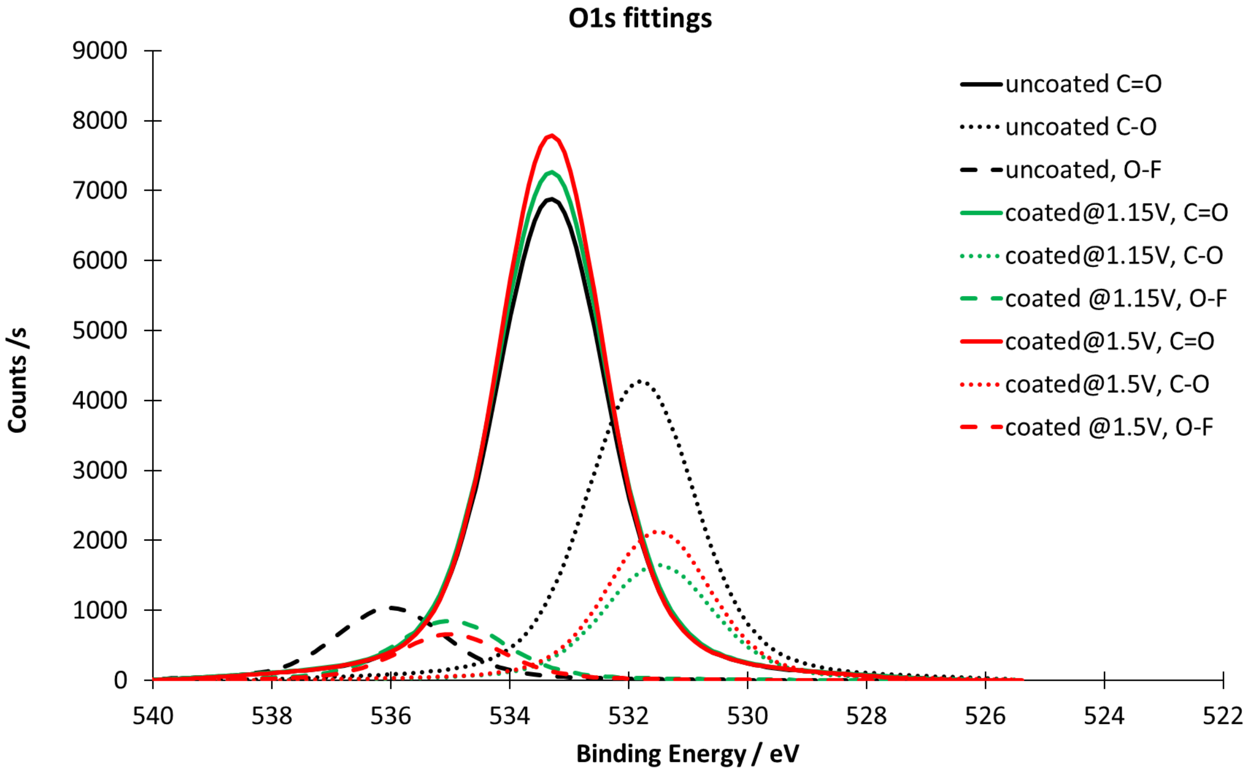
coated@1.5V, C-O-C
coated @1.5V, C-F
coated@1.5V, O-C=O

Results

XPS

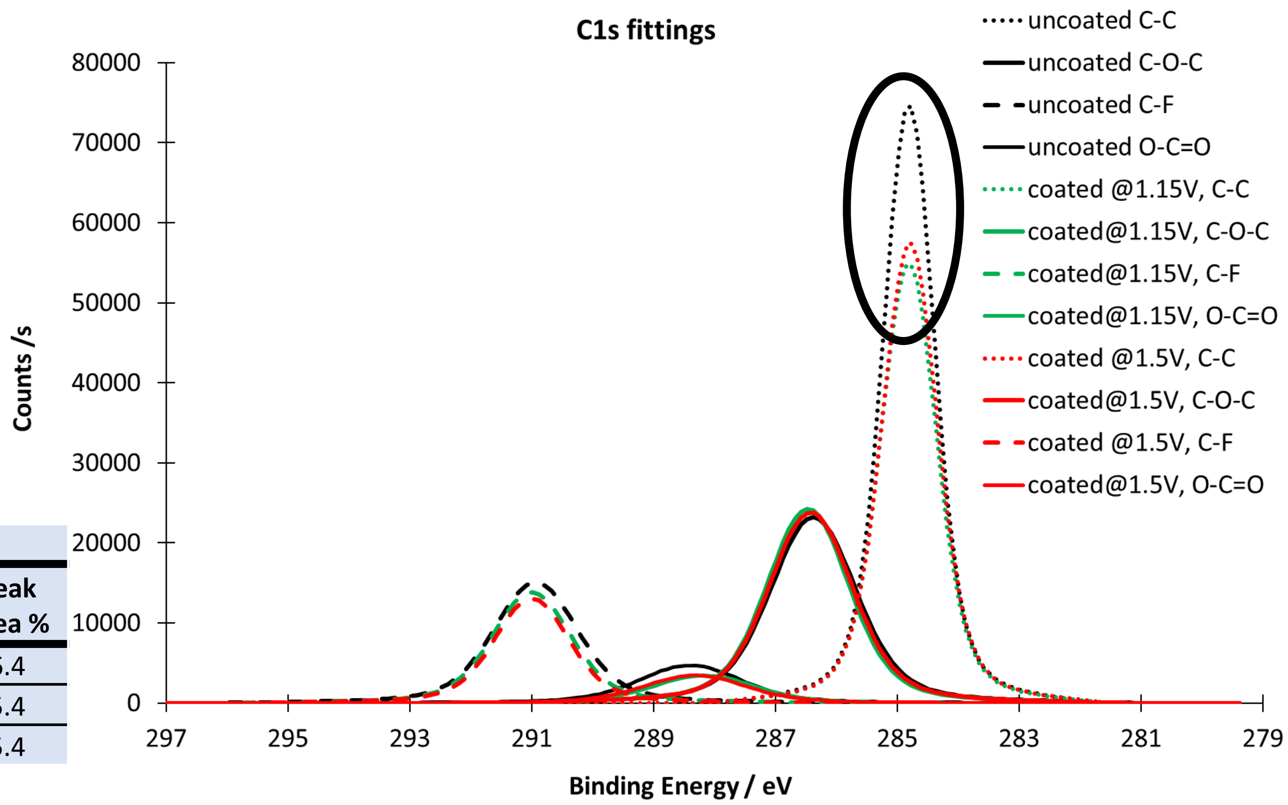


	C=O		O-F		C-O	
	Binding energy, eV	Peak Area %	Binding energy, eV	Peak Area %	Binding energy, eV	Peak Area %
uncoated	533.3	56.5	536.0	8.5	531.8	35.0
coated @1.15V	533.3	74.4	535.0	8.7	531.5	16.9
coated @1.5V	533.3	73.7	535.0	6.3	531.5	20.1

Results

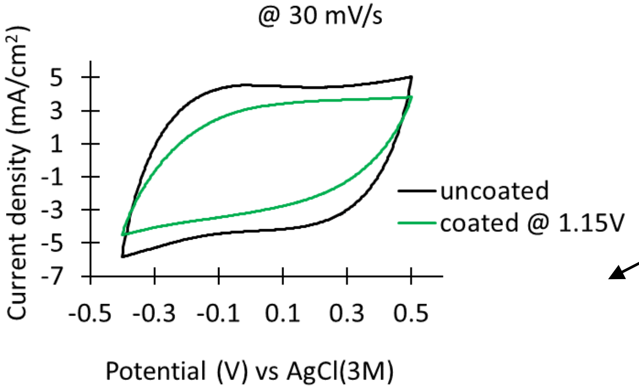
XPS

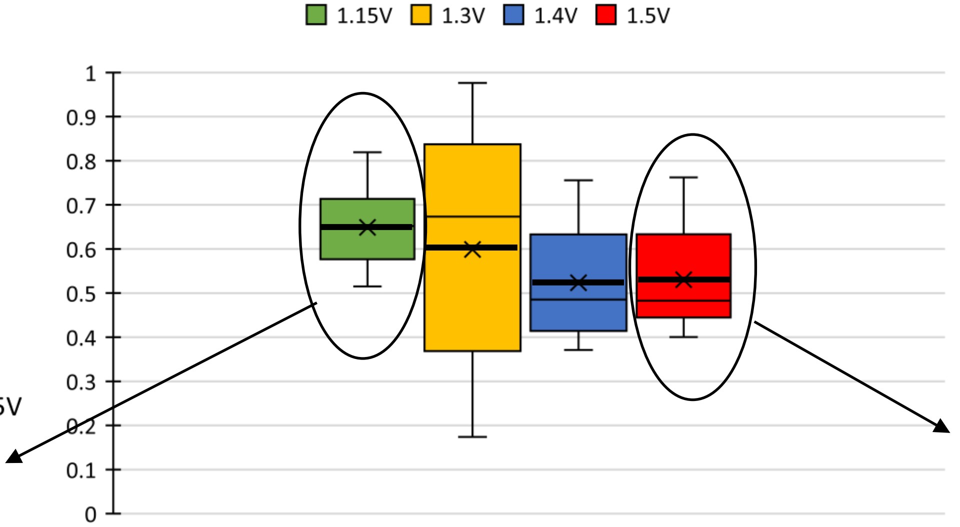
	C-C		C-O-C		C-F		O-C=O	
	Binding energy, eV	Peak Area %	Binding energy, eV	Peak Area %	Binding energy, eV	Peak Area %	Binding energy, eV	Peak Area %
uncoated	284.8	50.6	286.4	26.3	290.9	16.7	288.4	6.4
coated @1.15V	284.8	47.2	286.5	30.7	291.0	16.7	288.2	5.4
coated @1.5V	284.8	49.0	286.5	30.6	291.0	14.9	288.2	5.4

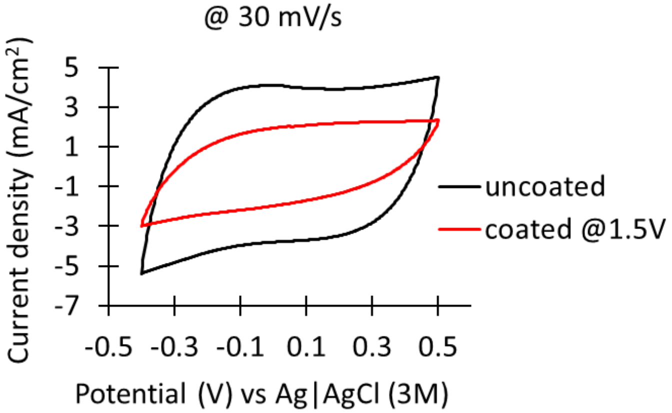


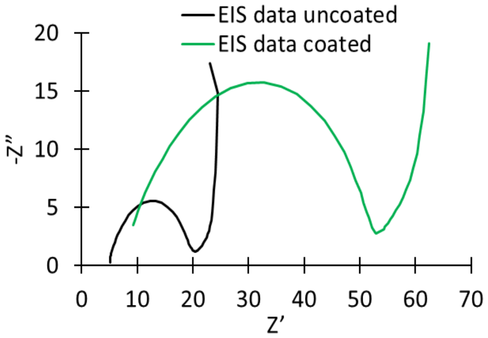
Results

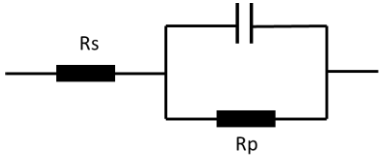
- Increasing the electropolymerization potential seems to slightly reduce the capacitance retention (65% @1.15V vs 55%@1.5V)
- The charge transfer resistance is almost 3x higher in the coated electrodes (43 Ω vs 15 Ω)

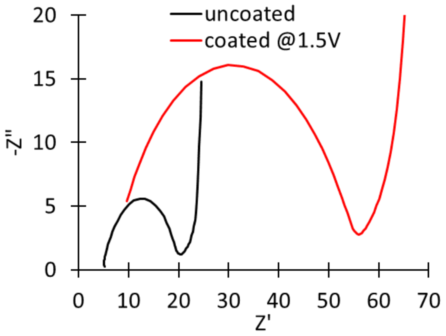




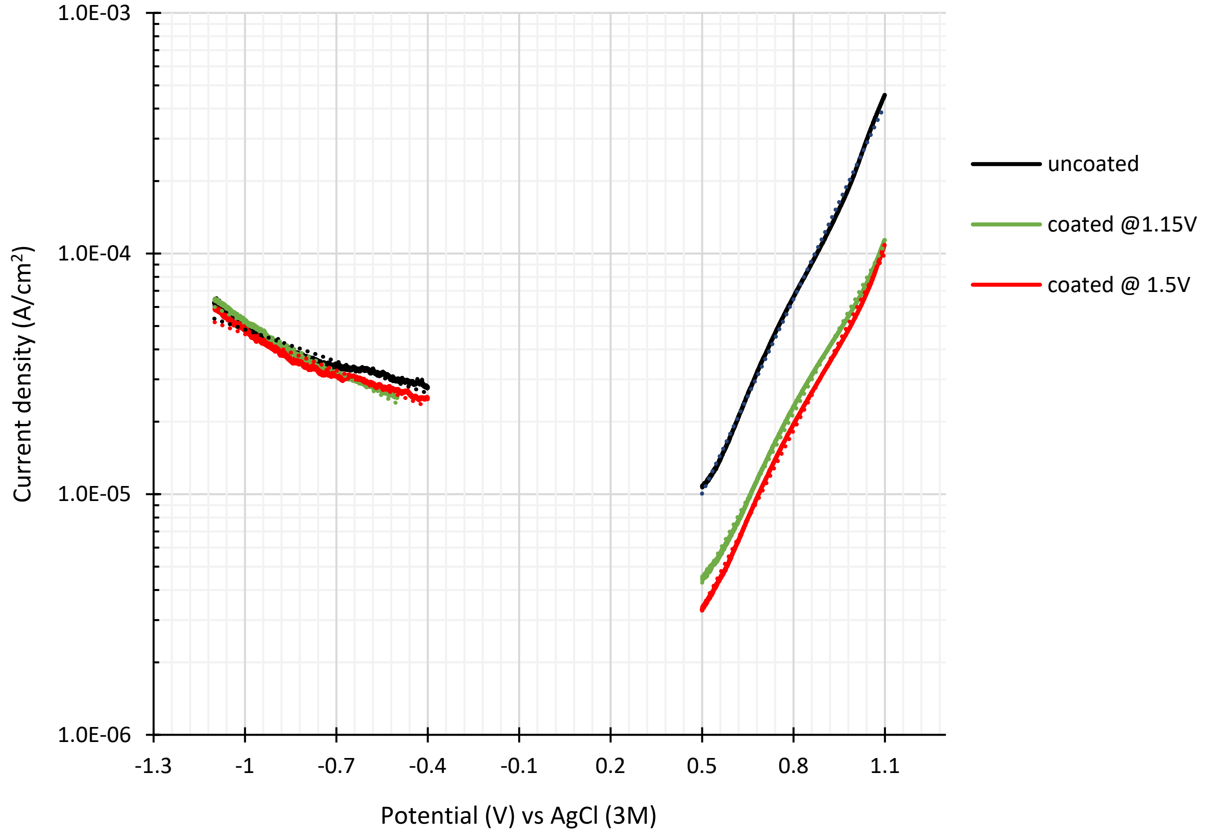








Results



exchange current density

$$i = i_0 e^{\beta\eta}$$

Tafel coefficient

Anodic currents

	$i_{0,}$ A/cm^2	β, V^{-1}
uncoated	4.5 x 10^{-7}	6.2
coated	2.9 x 10^{-7}	5.4

$$\log_{10}(i) = \beta \log_{10}(e)\eta + \log_{10}(i_0)$$

$$\log_{10}(i) = A\,\eta + B$$

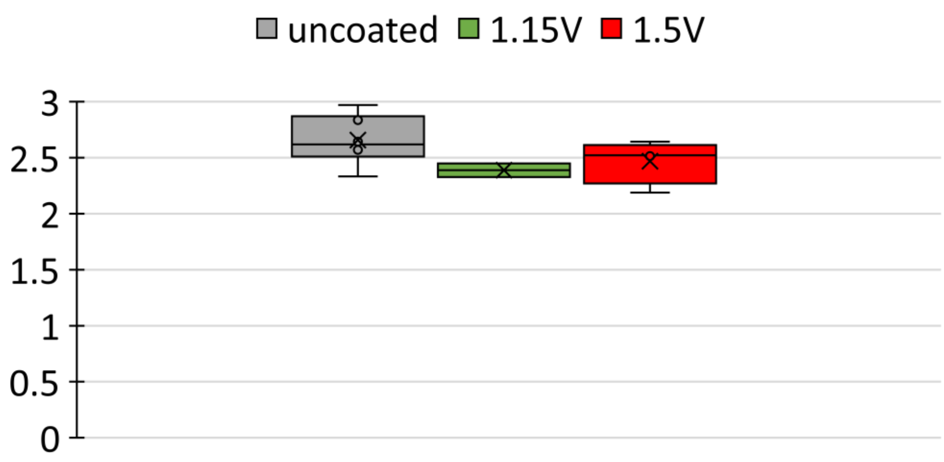
Results

$$\log_{10}(i) = \beta \log_{10}(e)\eta + \log_{10}(i_0)$$

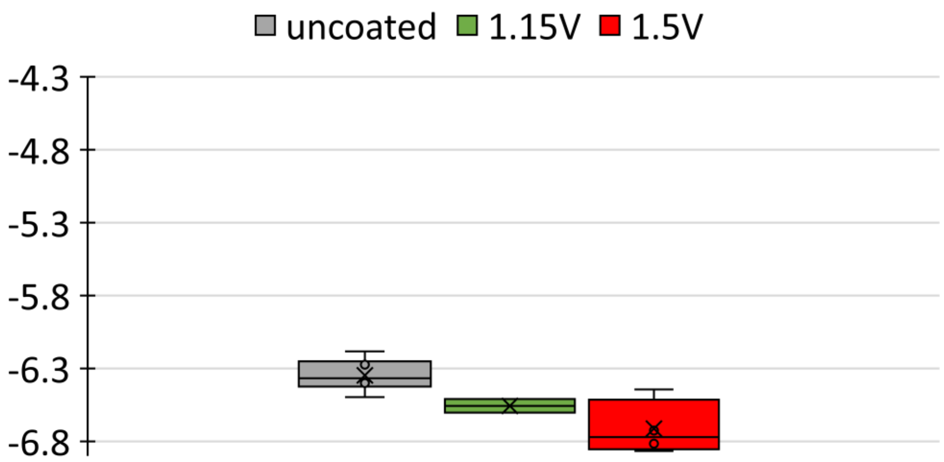
$$\log_{10}(i) = A\eta + B$$

- β and i_0 are lower for the coated electrodes

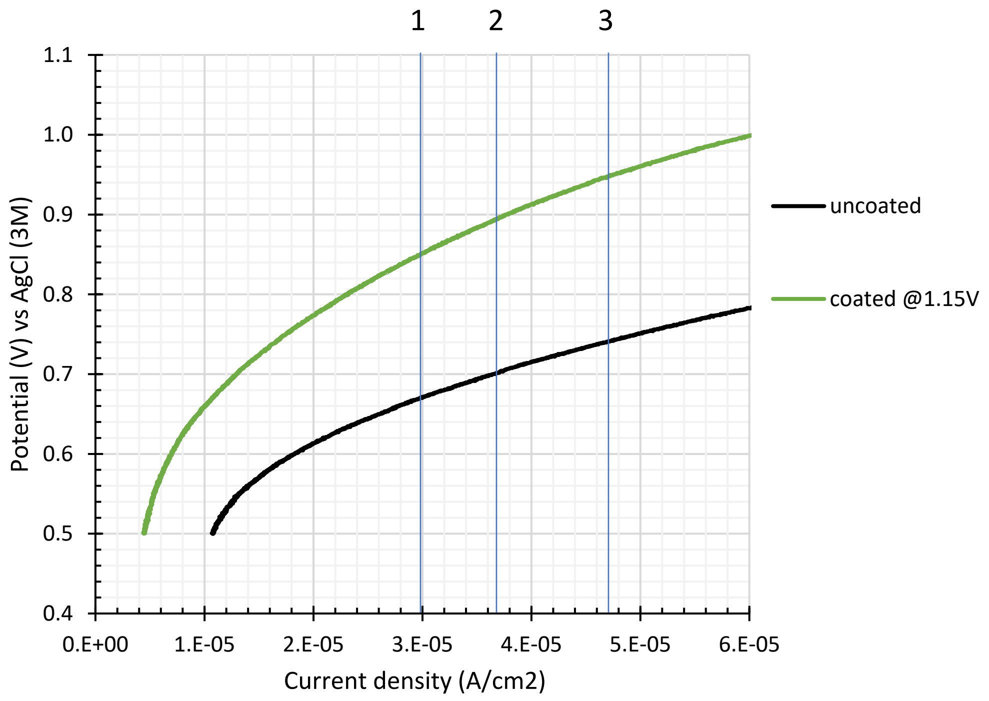
A



B



Results



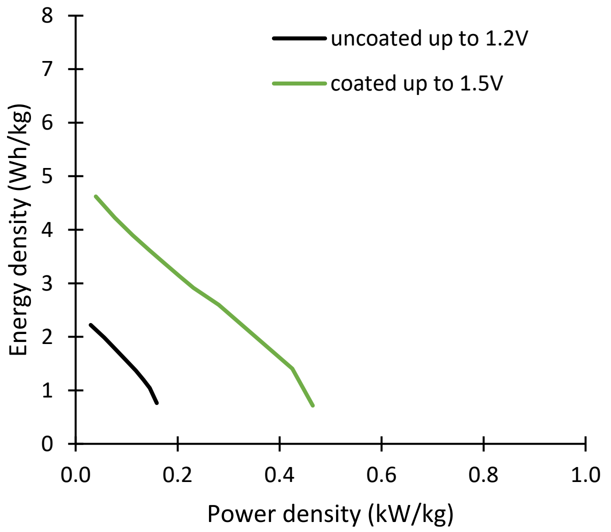
- For a same oxidation current, the maximum potential allowed is higher for the coated electrodes
- The maximum potential (E_{max}) corresponding to a current i can be obtained from the following equation:

$$E_{max} = \frac{\log_{10}(i\ ) - B}{A}$$

Results

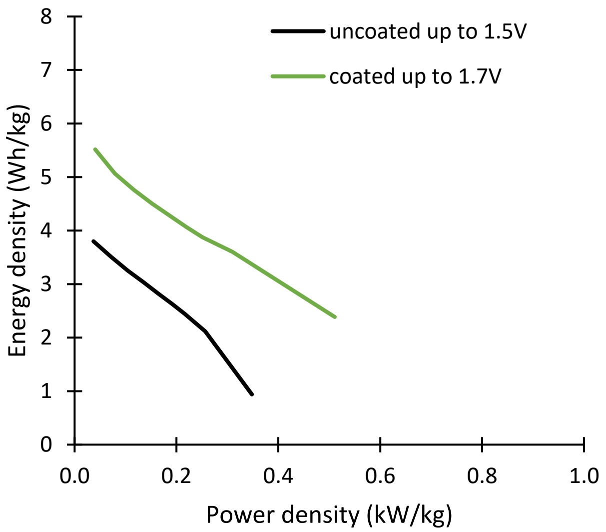
1: max current = 30 μA/cm²

	Uncoated	Coated
E_{max}	0.67	0.86
E_{min}	-0.51	-0.62
ΔV	**1.2**	**1.5**



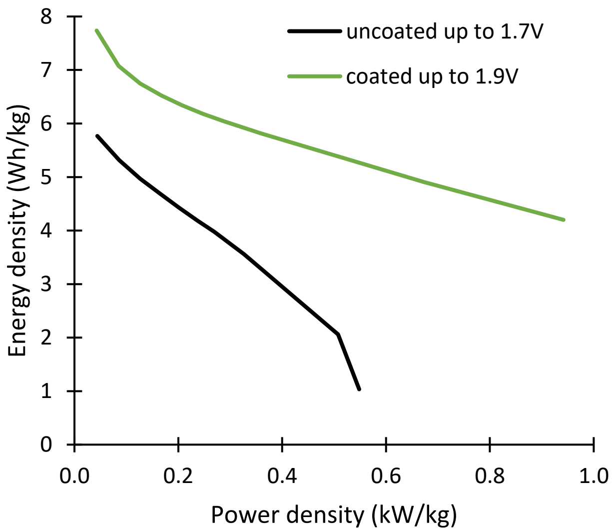
2: max current = 37 μA/cm²

	Uncoated	Coated
E_{max}	0.71	0.90
E_{min}	-0.74	-0.78
ΔV	**1.5**	**1.7**



3: max current = 47 μA /cm²

	Uncoated	Coated
E_{max}	0.75	0.94
E_{min}	-0.97	-0.94
ΔV	**1.7**	**1.9**



Conclusions

- The electrodeposition of PPO has a much higher impact on the suppression of anodic reactions
- Electrodepositing PPO on activated carbon electrodes partially suppresses the oxidative processes that limit the stable upper potential
- For a same parasitic current density, the voltage range allowed for a cell constructed with PPO-coated electrodes can be up to 25% higher, which results in higher energy and power densities

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Dr. G. Gaspar, IDL

Professor U. Wijayantha, Loughborough University

Professor K. Lobato, IDL

The authors declare no conflict of interests

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