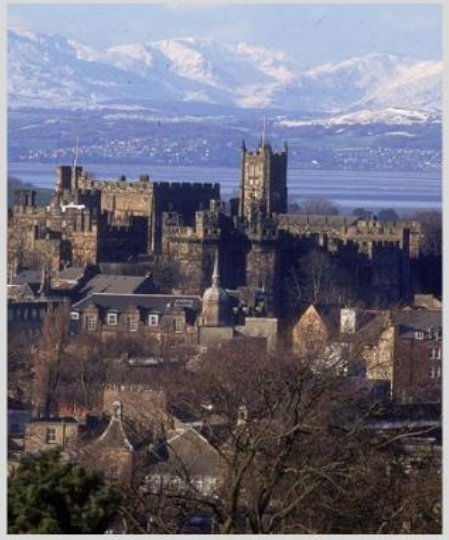
Real time detection of electrode side reactions by **on-line flow cell ICP-OES** One step closer to realising next generation batteries

Shahin Nikman, Beatrice Wolff, Harry Hoster



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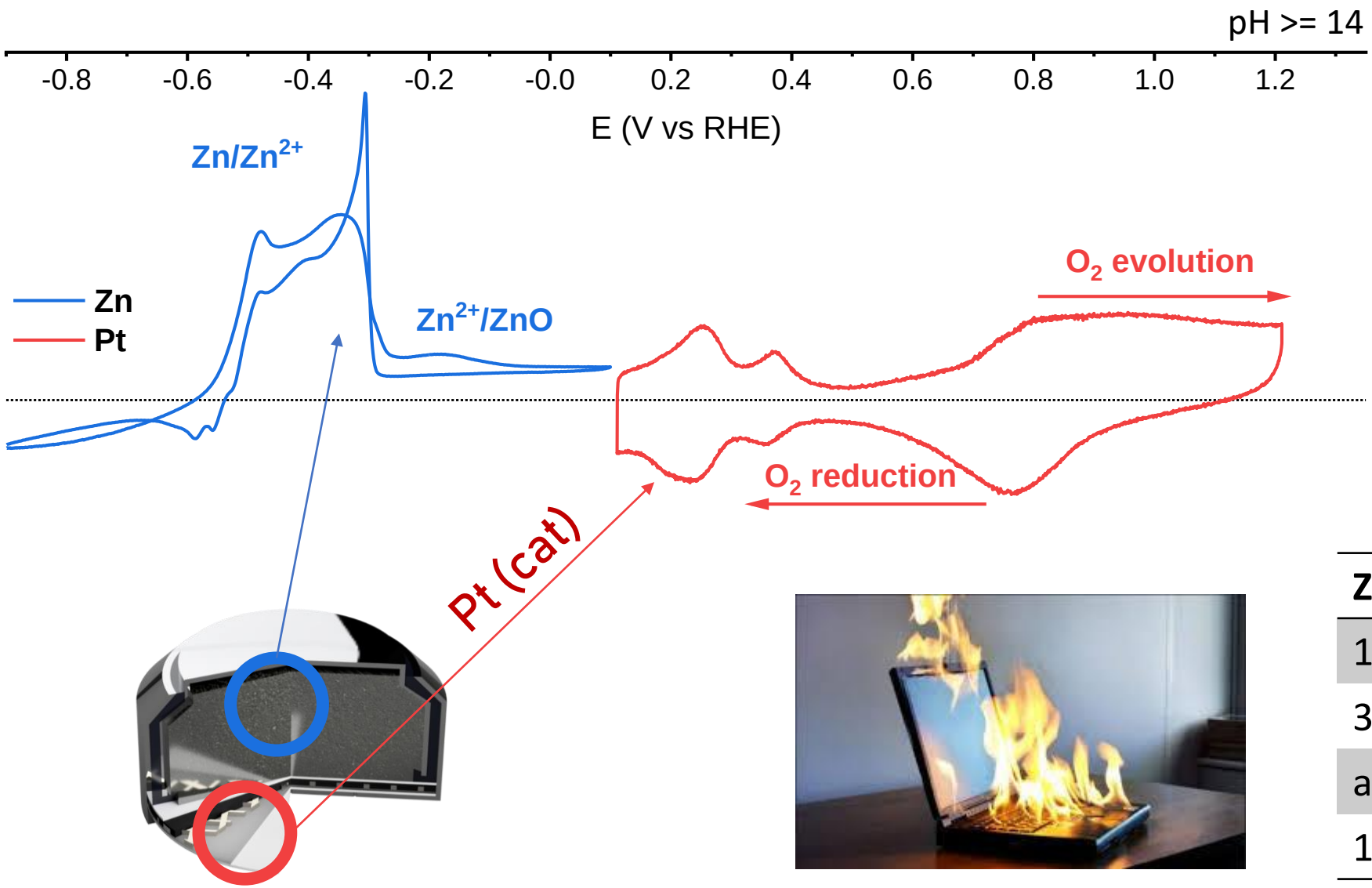
Zinc-Air Electrochemistry



$$Zn + 4OH^- \rightarrow ZnOH_4^{2-} + 2e^-$$

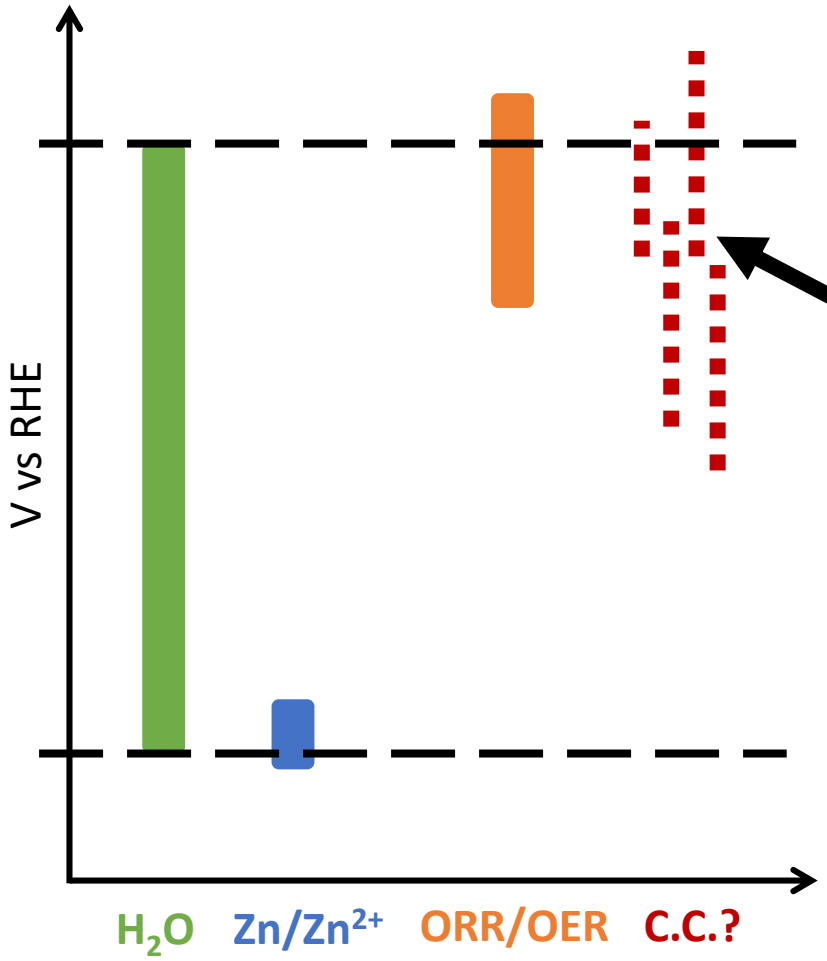
$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

$$ZnOH_4^{2-} \rightarrow ZnO(s) + H_2O + 2OH^-$$

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO(s)$$

Zn-air	Li-ion
1370 W h kg^{-1}	265 W h kg^{-1}
385 £/Ah	2500 £/Ah
aqueous	Organic
1.65 V	4.0 V

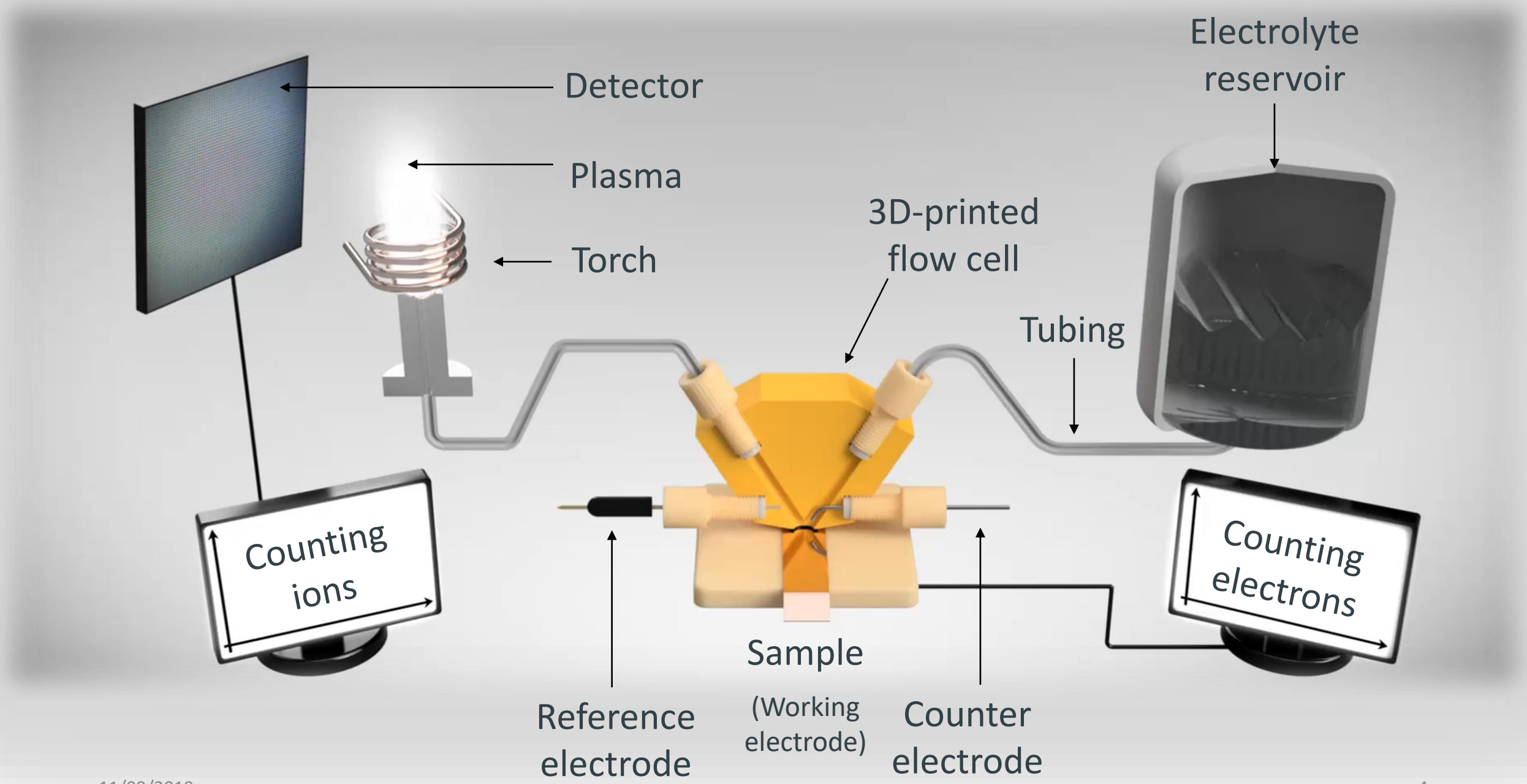
Voltage windows and parasitic side reactions



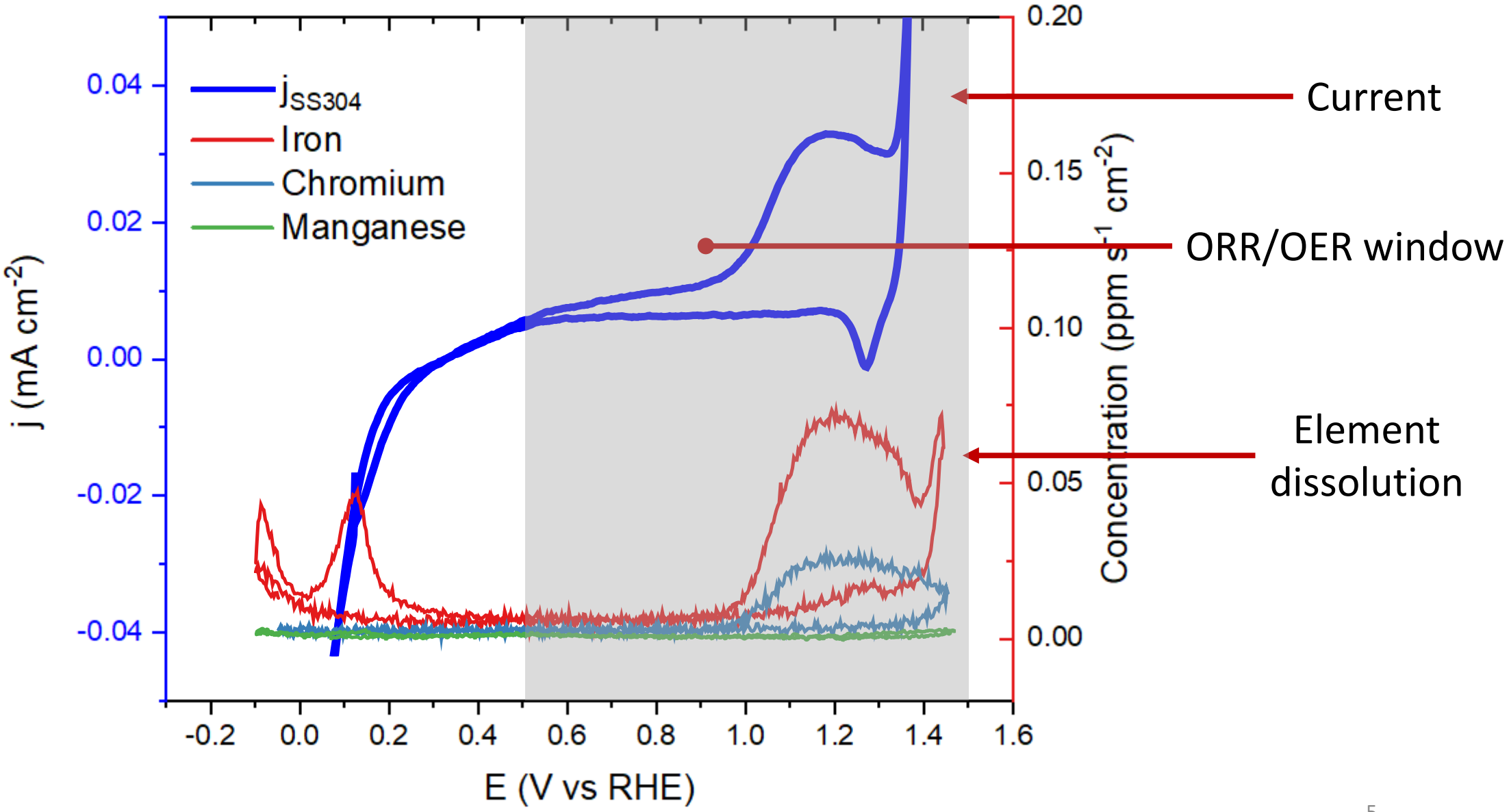
- H_2O electrochemical window
- **Negative** and **positive** electrode operational window
- **Current collector *inert* window**

Current Collectors
Stainless steels [1]
Nickel [2]
Titanium [3]
Silver [4]

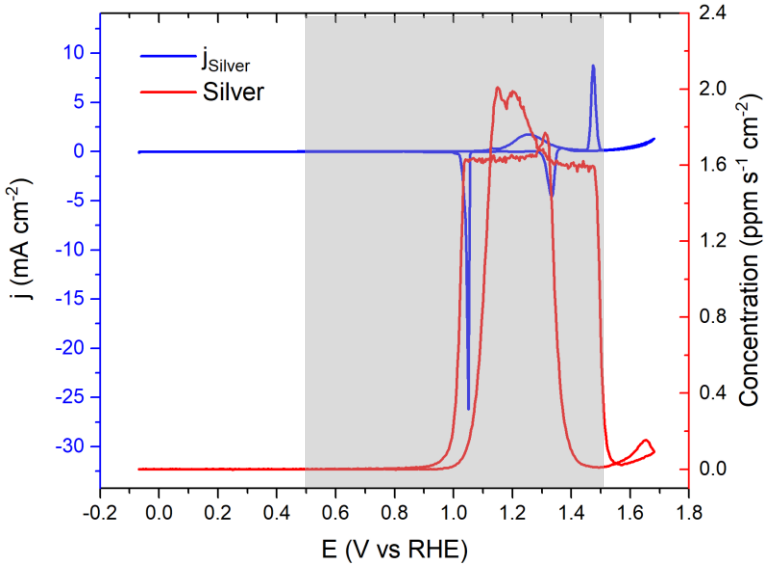
But for Li-ion only copper and aluminium is used!

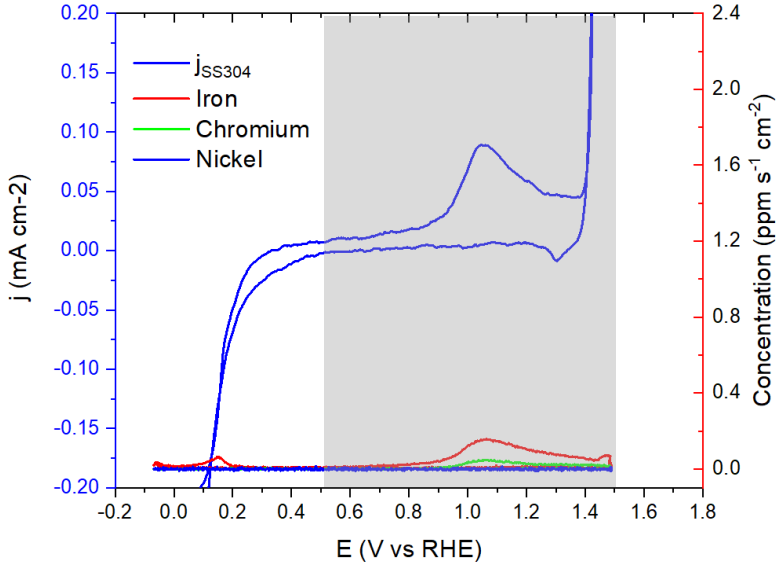

Detector
Plasma
Torch
3D-printed flow cell
Electrolyte reservoir
Tubing
Counting ions
Counting electrons
Reference electrode
Sample
(Working electrode)
Counter electrode

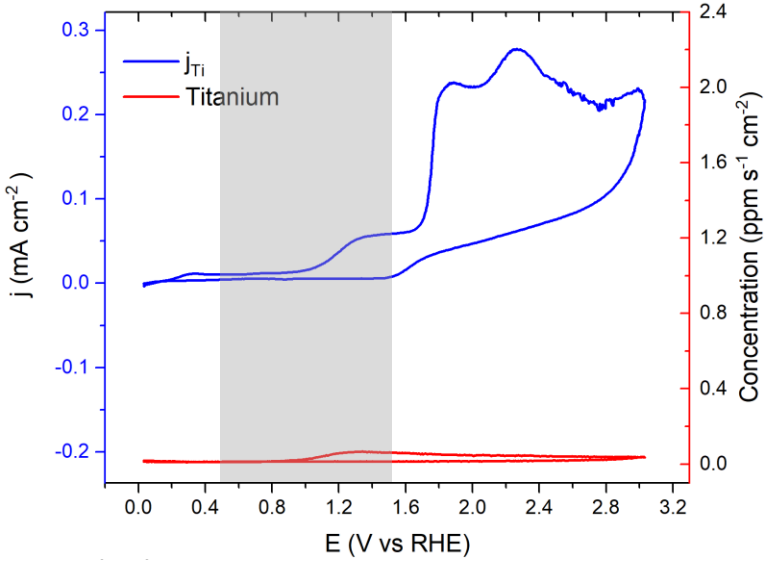
Results I – C.C. dissolution

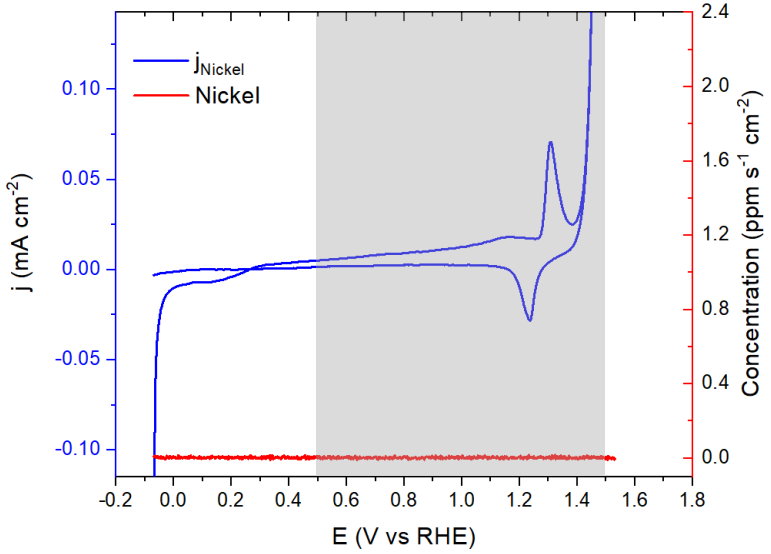


Results I – Current Collectors Dissolution





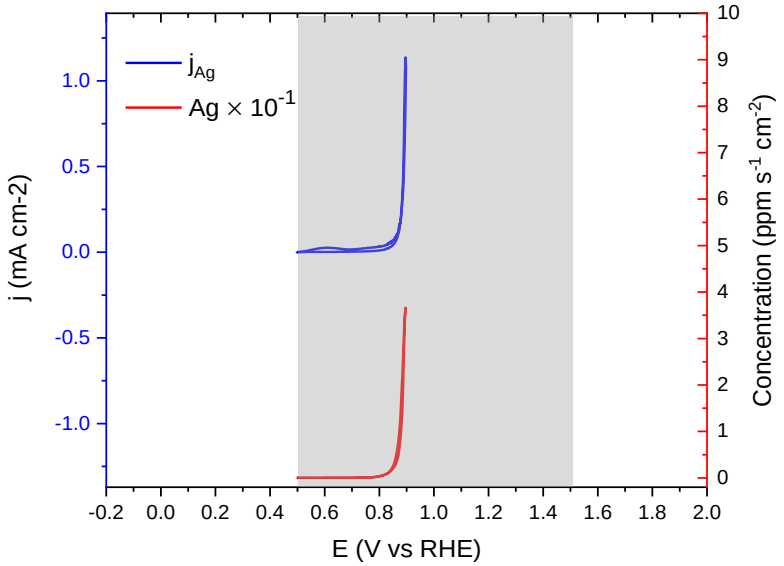


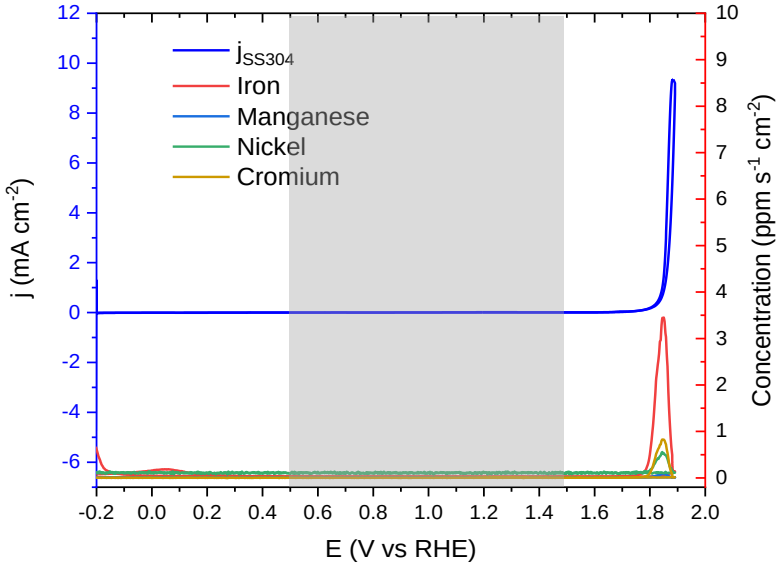


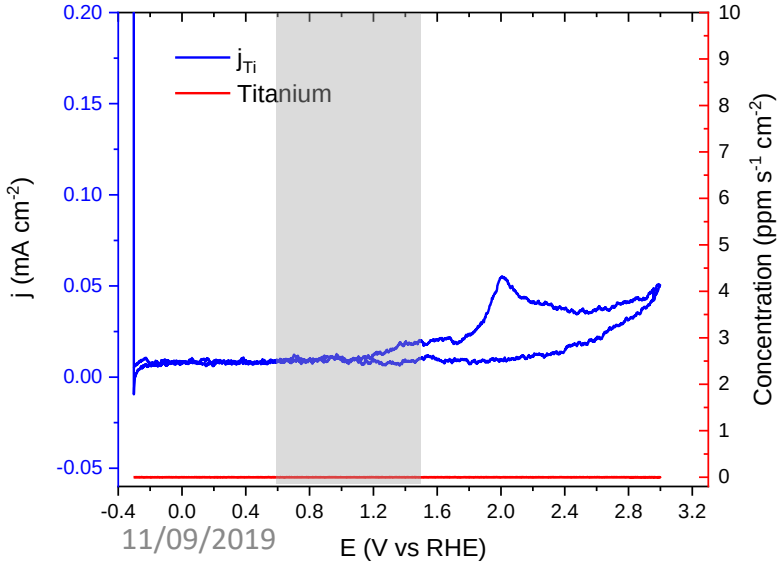
1.1) Silver
1.2) Stainless steels

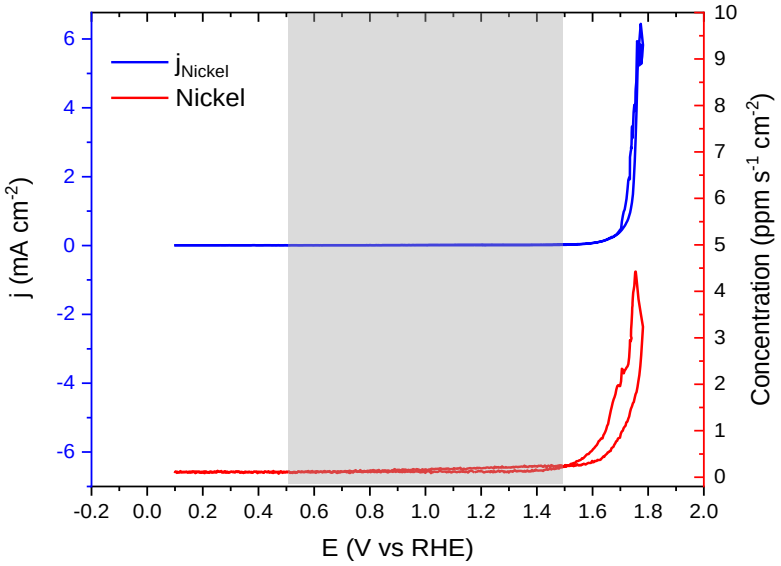
2.2) Titanium
2.2) Nickel

Results I – Current Collectors Dissolution









1.1) Silver
1.2) Stainless steels

2.2) Titanium
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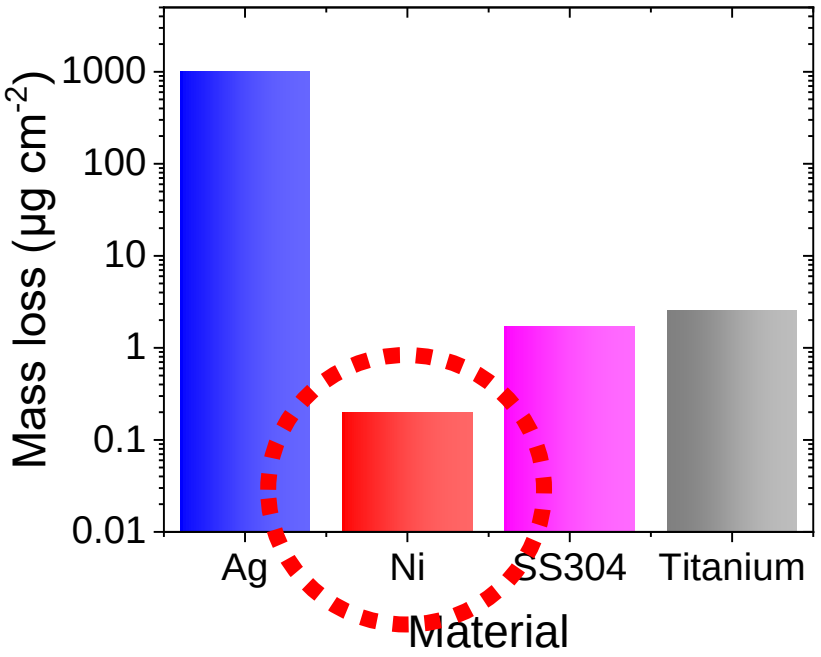
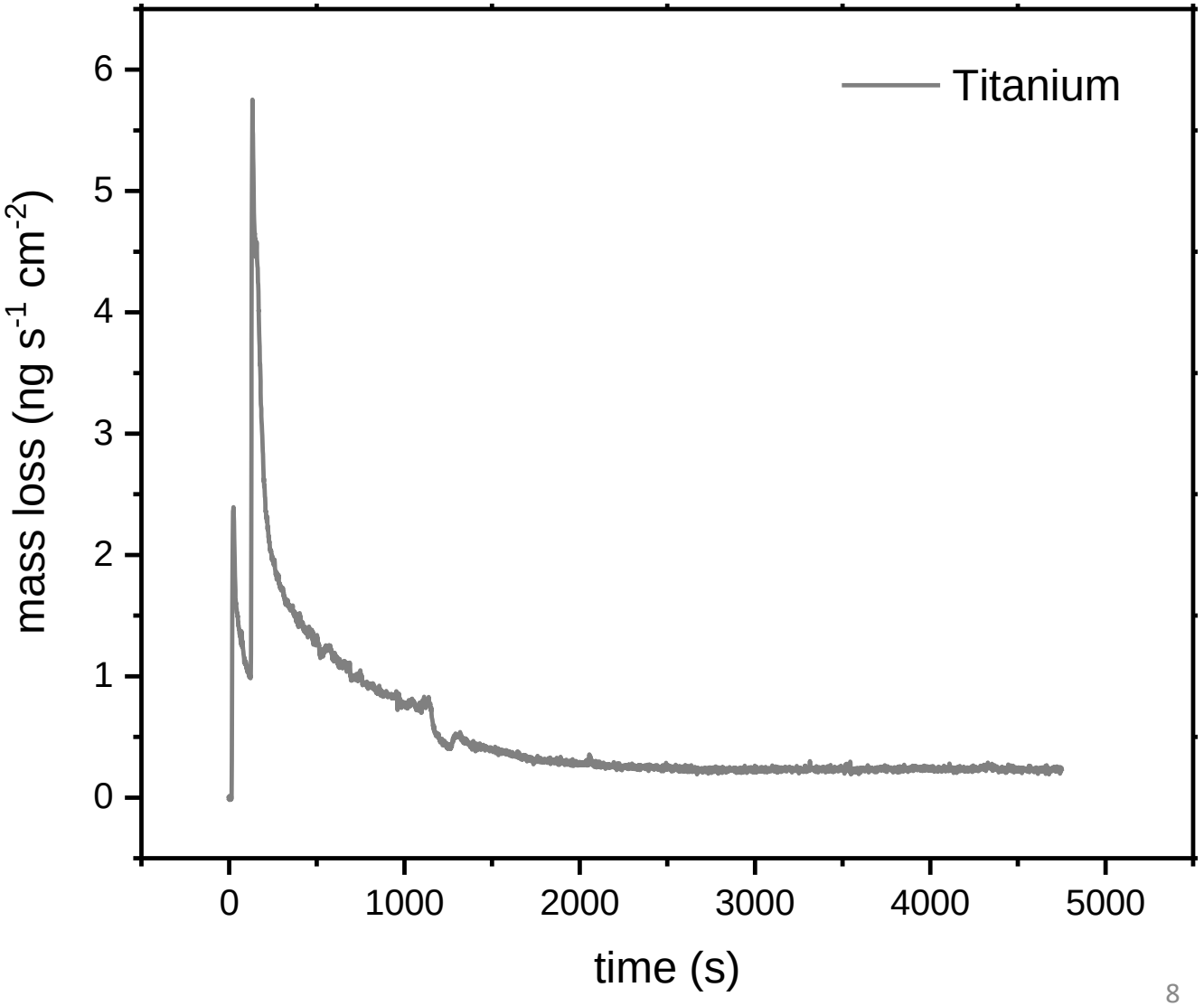
Results I – Current Collectors Dissolution

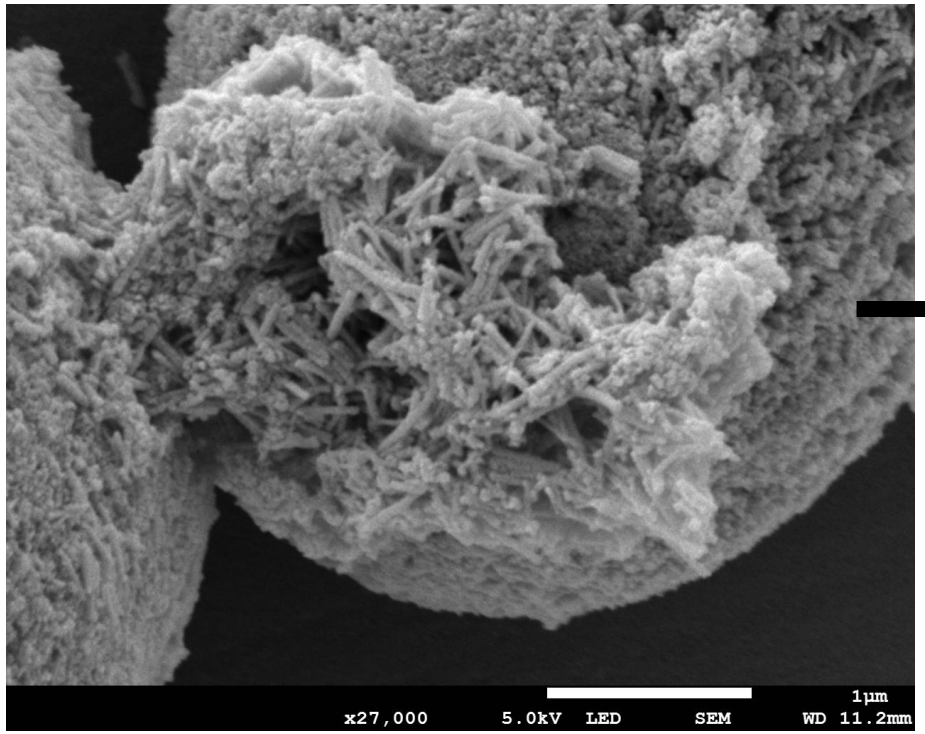
Simulate aggressive charging conditions

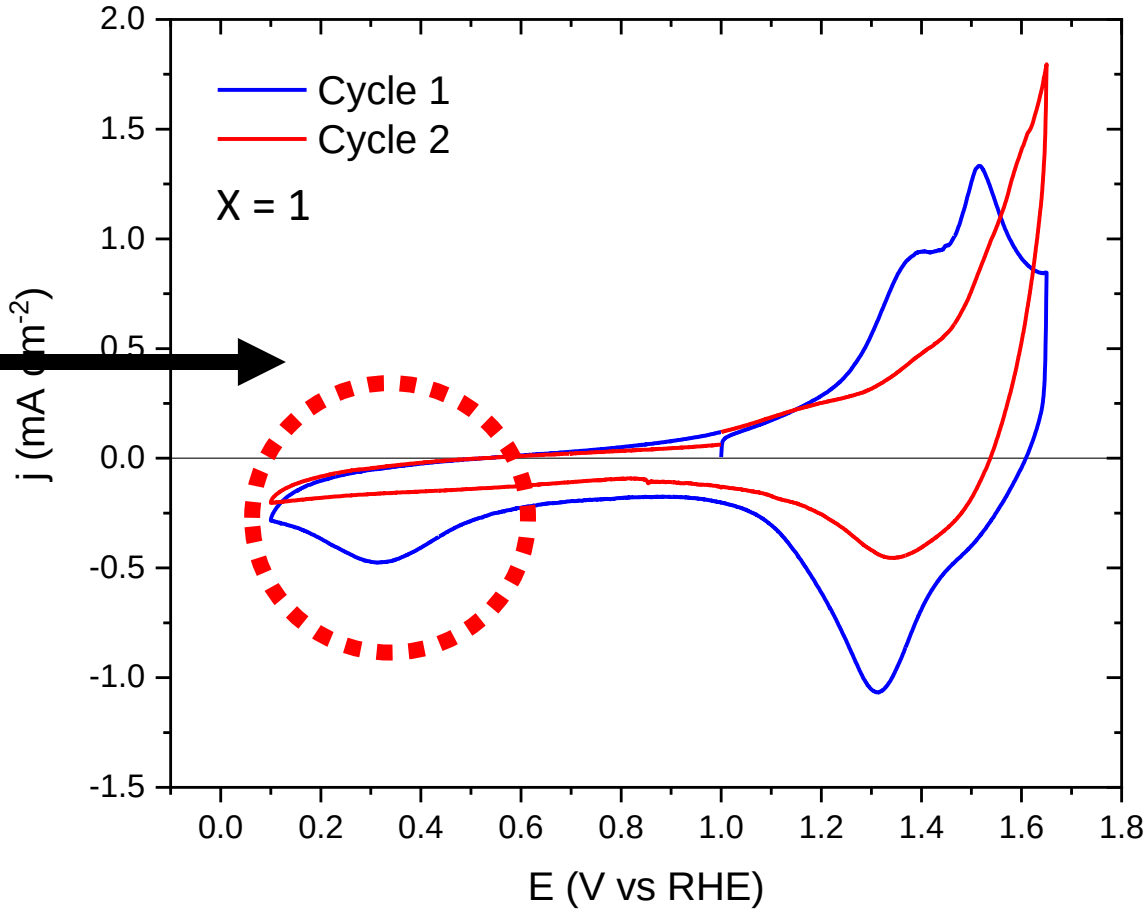
- 1 mA cm^{-2} anodic current
- 1 M KOH
- 1.5 mL min^{-1} flow



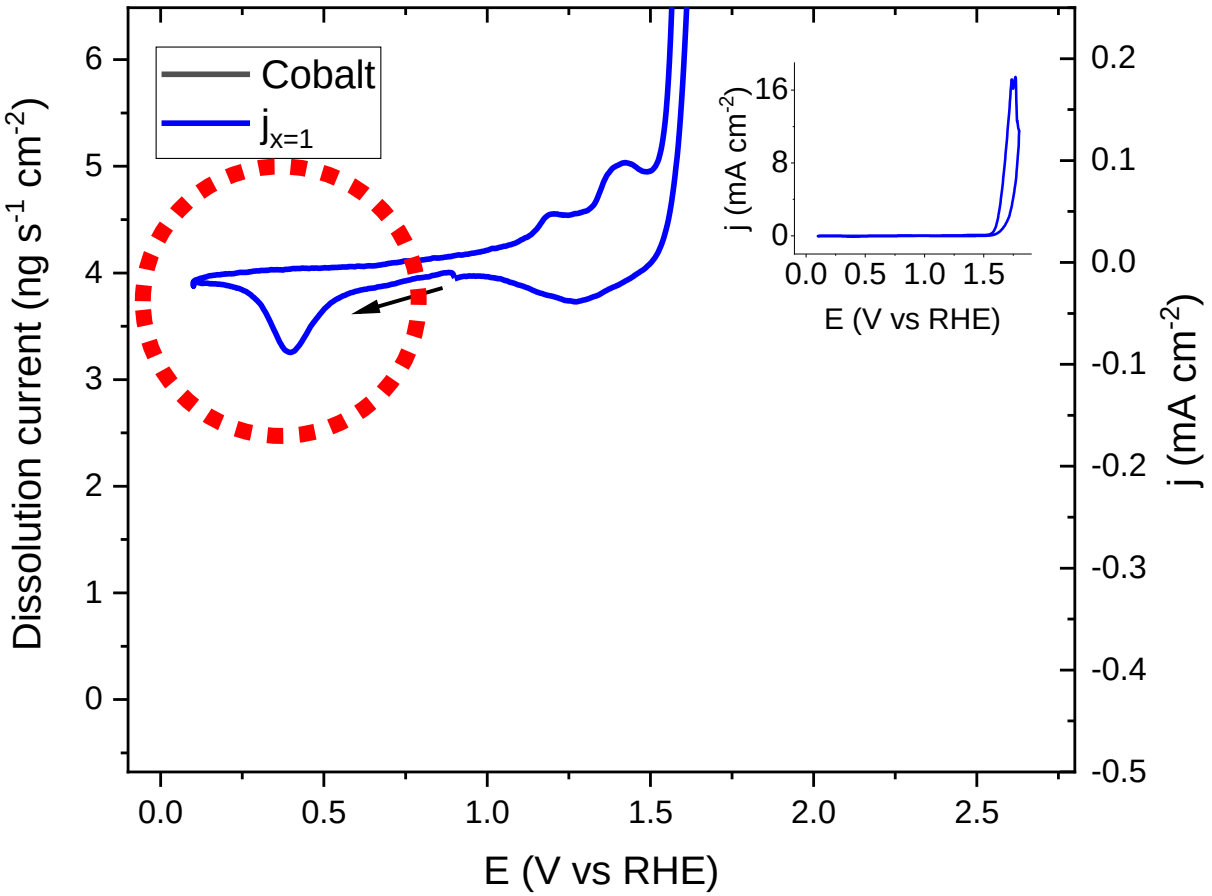


Results II - Stability of $Ni_xCo_{3-x}O_4$





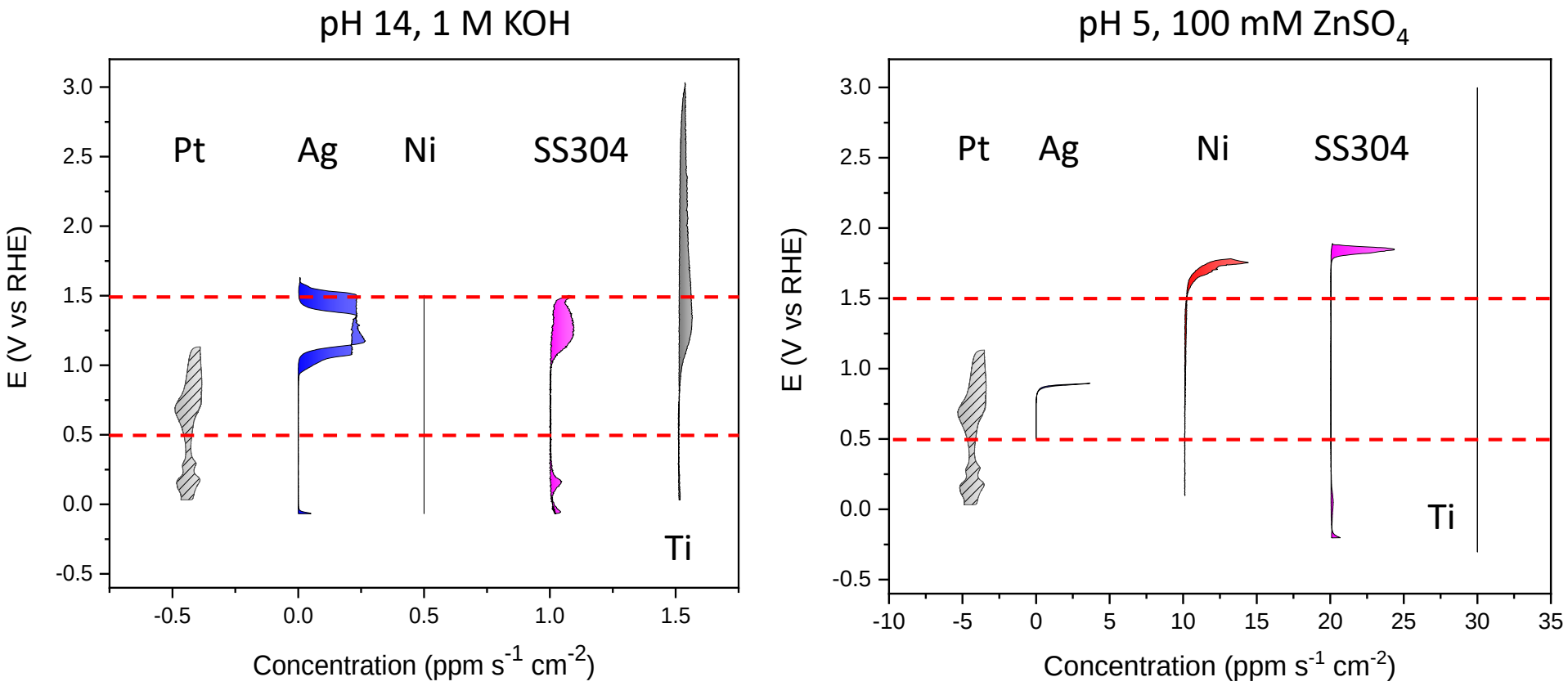
Results II - Stability of $Ni_xCo_{3-x}O_4$



x in $Ni_xCo_{3-x}O_4$	µg cm^{-2}
0	0.049
0.4	0.48
0.5	0.53
0.8	**0.80**
1.0	0.42

Conclusion

- Nickel most stable positive current collector for alkaline zinc-air cells
- Nickel cobalt oxides unstable under high discharge conditions
- Instability of nickel cobalt oxide increase with Ni substitution
- Stability window must be considered for all materials



AMAZONAS HAS DECLARED EMERGENCY STATE

Thank you for your attention

References:
[1] D. Pletcher et al, *Electrochim. Acta*, 2016, **188**, 286–293.
[2] Z. Ma et al, J. Power Sources. 274 (2015) 56–64. doi:10.1016/j.jpowsour.2014.10.030.3
[3] M. Xu, et al, J. Power Sources. 283 (2015) 358–371. doi:10.1016/j.jpowsour.2015.02.114.
[4] D. Wittmaier et al, Adv. Energy Mater. 5 (2015) 1–8. doi:10.1002/aenm.201500763.