BATTERY CONFERENCE
March 28-30, 2022

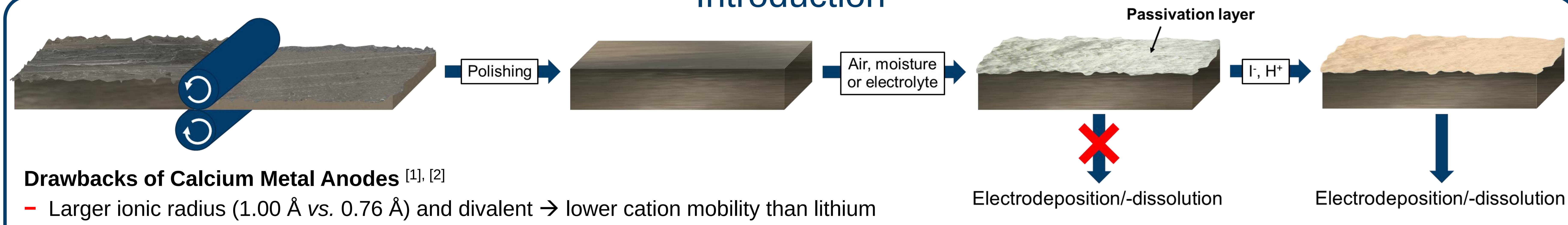
JÜLICH Forschungszentrum | HELMHOLTZ-INSTITUT MÜNSTER

# Borate-Free Electrolytes for Calcium Metal Batteries


J. Wellmann[a], M. Winter[a,b], E. Paillard[c]

[a] Helmholtz-Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany
[b] MEET Battery Research Center, Institute of Physical Chemistry, University of Münster, Corrensstraße 46, 48149 Münster, Germany
[c] Politecnico di Milano, Department of Energy, Via Lambruschini 4, 20156 Milan, Italy


## Introduction




**Drawbacks of Calcium Metal Anodes** [1], [2]

− Larger ionic radius (1.00 Å *vs.* 0.76 Å) and divalent → lower cation mobility than lithium
− Strongly insulating passivation layer prevents reversible electrodeposition/-dissolution
− Decomposition reactions with common electrolytes

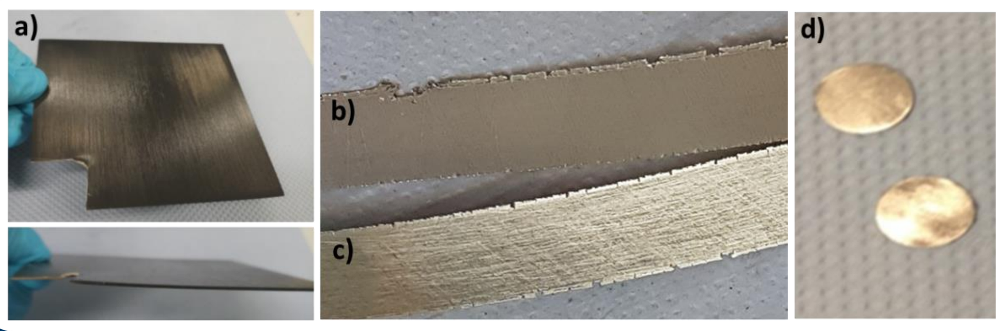
**Advantages of Calcium Metal Anodes** [1], [2]

+ Lower potential than most other metals (−2.87 V *vs.* SHE)
+ High theoretical volumetric capacity (2072 mAh cm$^{-3}$)
+ Less prone to dendrite formation than lithium
+ 5$^{th}$ most abundant element in earth crust

**Motivation** [1], [2]

- $MgCl_2$ is known to shield magnesium surface against water and other impurities
- $CaCl_2$ has low solubility and $Ca^{2+}$ is larger than $Mg^{2+}$
  → $CaI_2$ should have a similar effect on the calcium surface
- Etching additives might prevent passivation of calcium surface

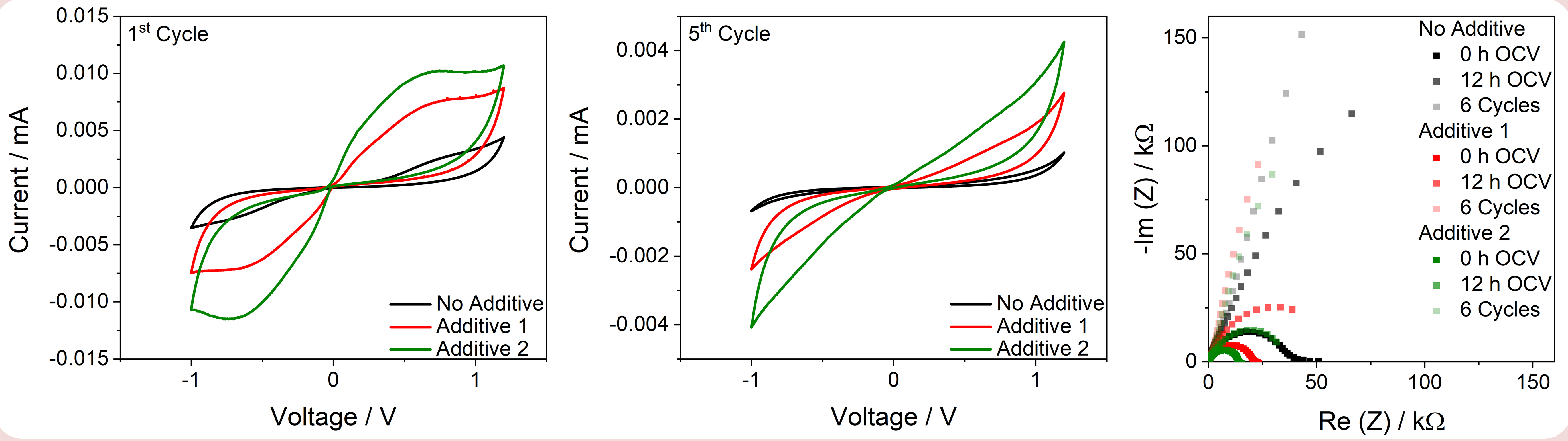
## Experimental




a) As-received (1 mm)
b) Roll-pressed (100 µm)
c) Polished
d) Washed electrodes

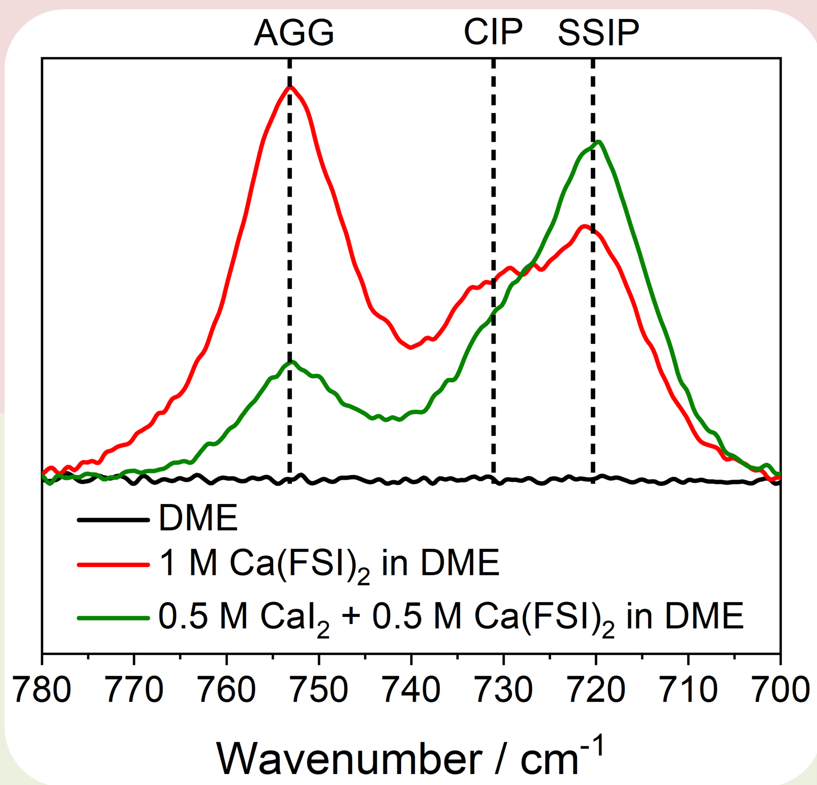
Coin Cell 2032, 20 °C, WE: Ca (Ø 12 mm), CE: Ca (Ø 12 mm)
Separator: Whatman GF/A (Ø 16 mm), Scan rate: 0.1 mV/s
Electrolyte: → Upper graphs: 100 µL (**1 M $Ca(FSI)_2$ in DME**)
→ Bottom graphs: 100 µL (**0.5 M $CaI_2$ + 0.5 M $Ca(FSI)_2$ in DME**)

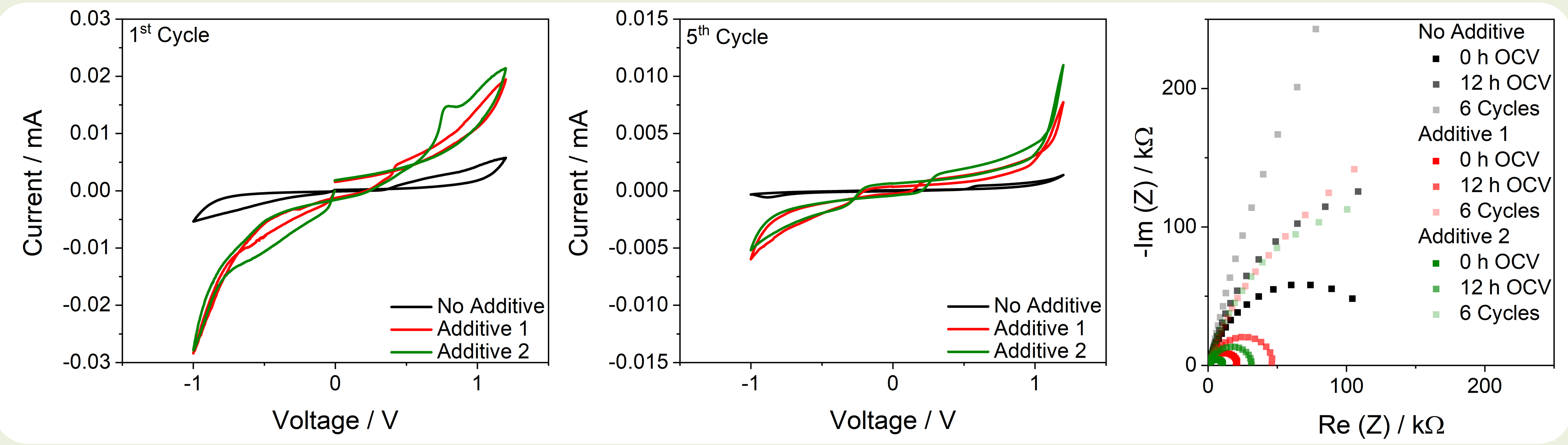
## Results & Discussion




**Without $CaI_2$**

- Additives (especially 2) decrease impedance before cycling and increase current during cycling
- Similar impedance after cycling
- Changing direction of scan leads to fast drop in current




**With $CaI_2$**

- Additives (especially 2) decrease impedance (even after cycling)
- Higher current in general, no sudden drop after changing scan direction
- Addition of $CaI_2$ leads to change in coordination of $FSI^-$

## Conclusion

Addition of $CaI_2$ and etching additives improves performance

- Decreased impedance (even after cycling) & higher current flow during cycling
- After 5 cycles still higher current flow than in the initial one without → Slower passivation
- Weaker coodination between $Ca^{2+}$ and $FSI^-$

## Acknowledgement


VIDICAT

The authors would like to acknowledge financial support by the European Union´s Horizon 2020 research and innovation programme within the project "VIDICAT" under grant agreement number 829145.


Mitglied der Helmholtz-Gemeinschaft


[1] A. Ponrouch *et al*. *Energy Storage Materials* **2019,** *20*, 253-262.
[2] D. Wang *et al*. *Nature Materials* **2018,** *17* (1), 16-20.



ju.wellmann@fz-juelich.de