About the role of copper in moisture sensitivity of high-entropy O3-type Na-layered oxides

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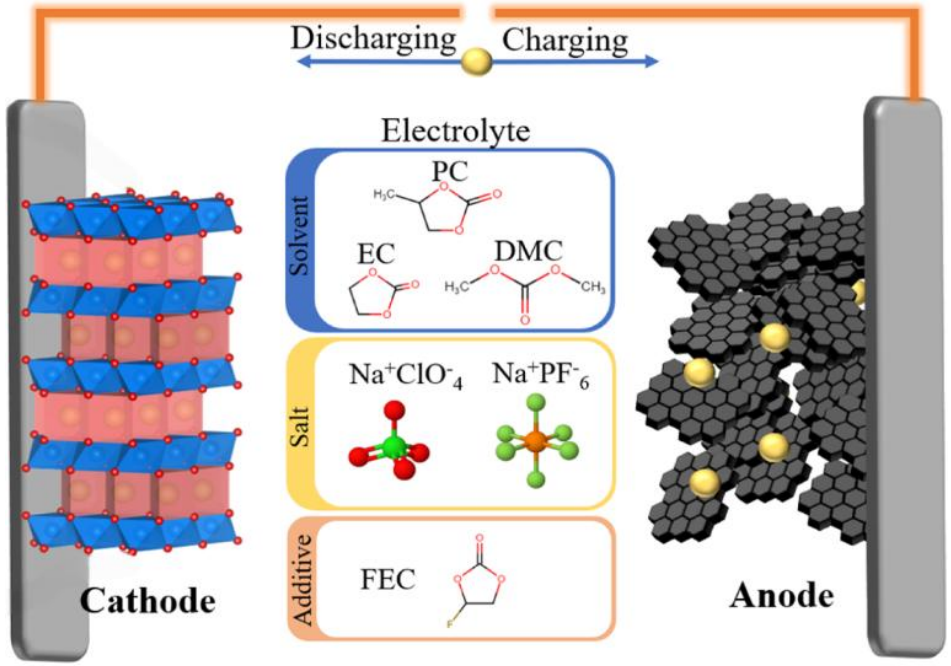
Group for applied materials and electrochemistry

Energy storage systems

Na Ion Batteries

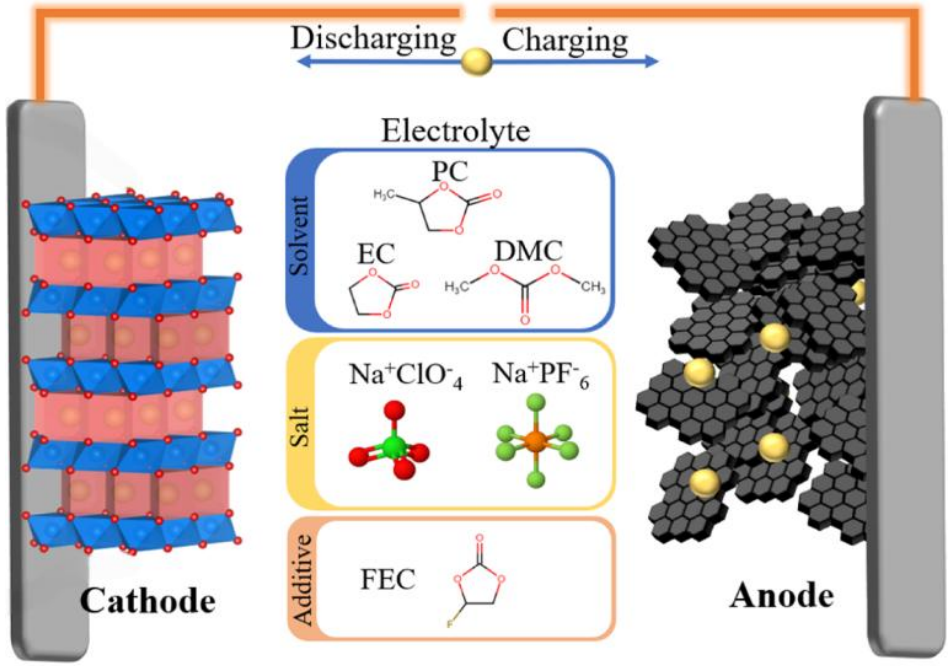


Schematic representation of a battery

Wei, G.-X. *et al.*, *Energy Storage Materials* **2026**, *86*, 104957
Wong, K. H. *et al.*, *Energy Storage Materials* **2024**, *71*, 103549

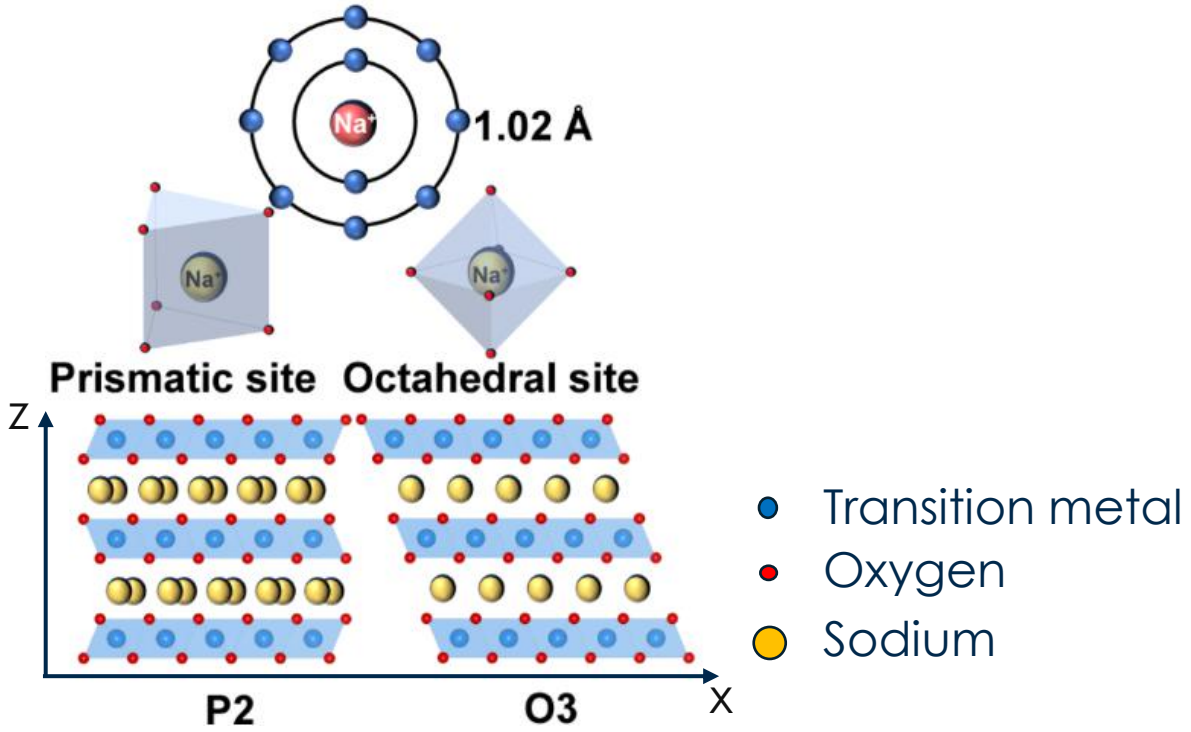
Energy storage systems

Na Ion Batteries



Schematic representation of a battery

Sodium Layered Oxide



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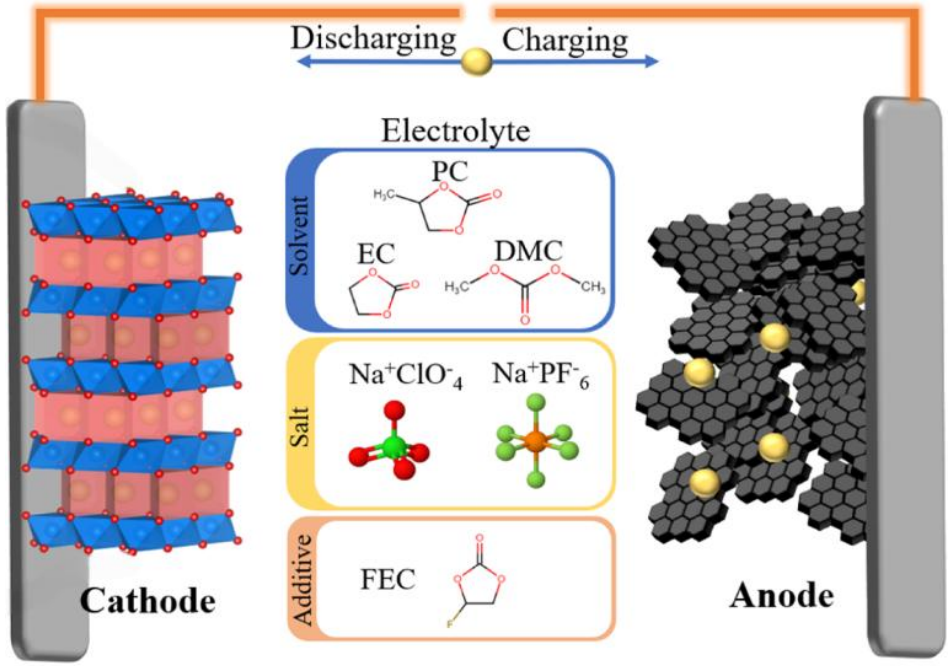
Energy storage systems

Na Ion Batteries



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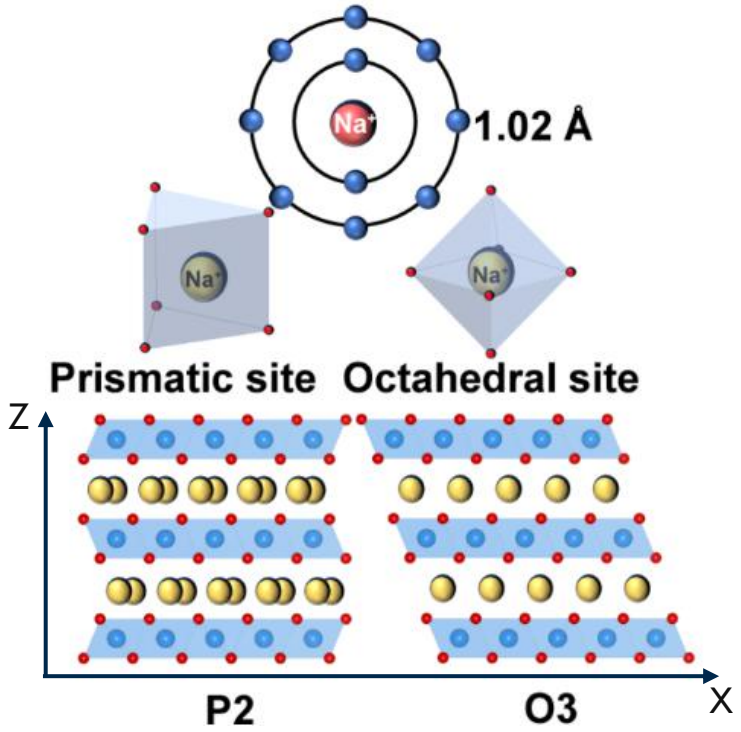

- High Theoretical Capacity
- Low diffusion kinetic of Na^+
- Phase transition above 4 V
- Moisture sensitivity

- Transition metal
- Oxygen
- Sodium

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Aim of the research

O3-type Sodium Layered Oxide:

- Enhanced structural stability at high voltages;
- Investigation of the reversibility of phase transition and related redox processes;
- Improved structural stability under moisture exposure;
- Identification of the key factors governing structural and electrochemnical stability.

Material selection and synthesis

Pristine: $Na_{0.83}[Ni_{0.33}Mn_{0.17}Fe_{0.17}Ti_{0.33}]O_2$

Hashimoto, K. *et al.*, *Inorg. Chem.* **2024**, *63* (49), 23317–23327

Material selection and synthesis

Pristine: $Na_{0.83}[Ni_{0.33}Mn_{0.17}Fe_{0.17}Ti_{0.33}]O_2$

Doped: $Na_{0.93}[Ni_{0.33}Mn_{0.12}Fe_{0.12}Ti_{0.33}Cu_{0.1}]O_2$

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Solid state synthesis

Precursors

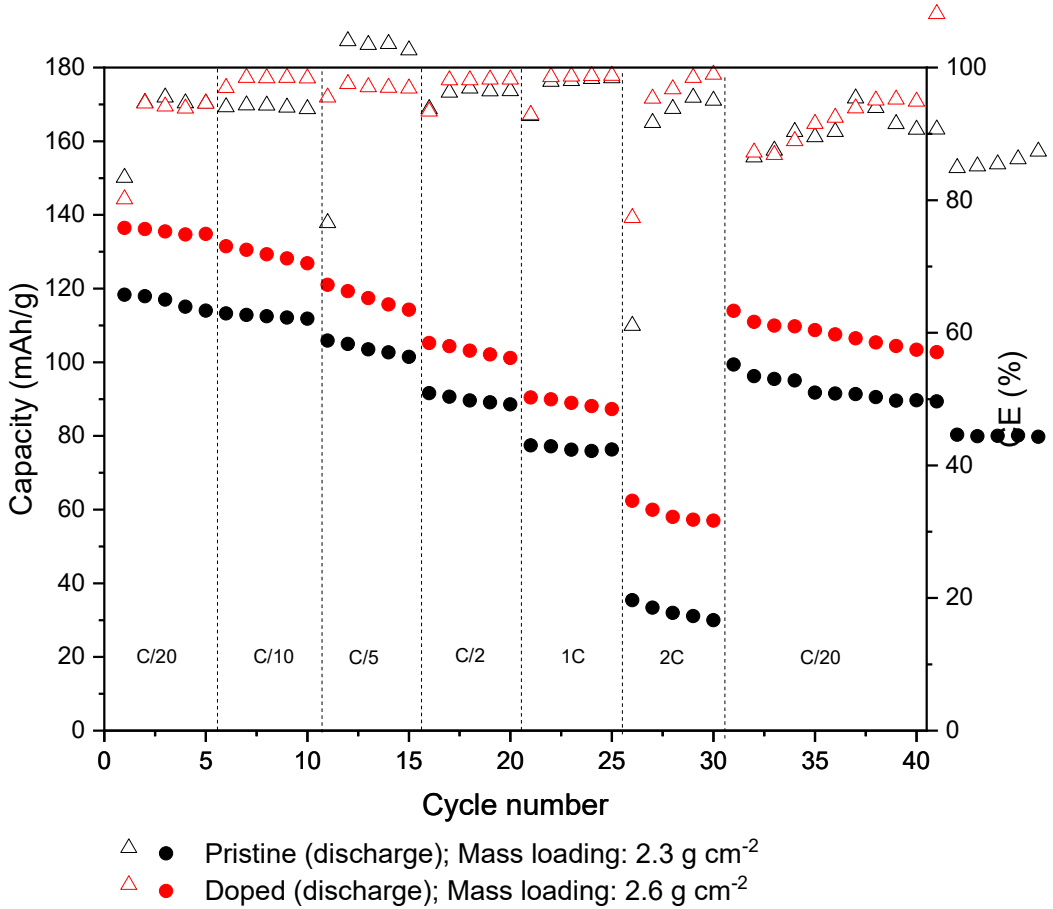
Na_2CO_3
NiO
Mn_2O_3
Fe_2O_3
TiO_2
CuO

Grinded in mortar and pelletized → **Synthesis in oven at 850 °C for 24 h** → **Liquid N_2 quenching**

Hashimoto, K. *et al.*, *Inorg. Chem.* **2024**, *63* (49), 23317–23327

Preliminary electrochemical characterization

Rate Capability test 2-4 V

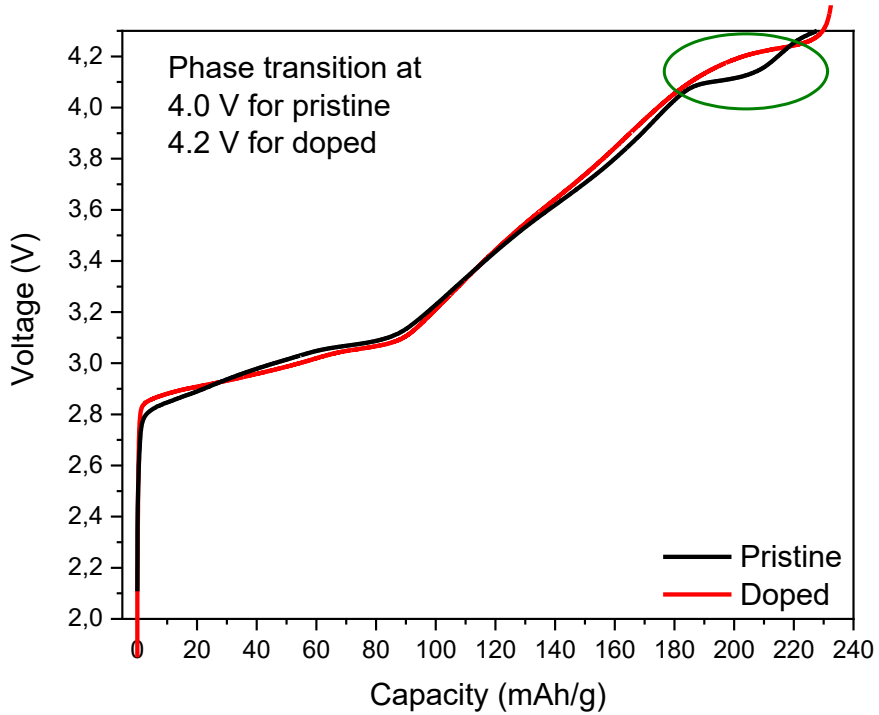


Total capacity:
Pristine: 118 mAh g^{-1}
Doped: 136 mAh g^{-1}

Capacity Retention after 40 cycles:
Pristine: 76%
Doped: 76%

Preliminary electrochemical characterization

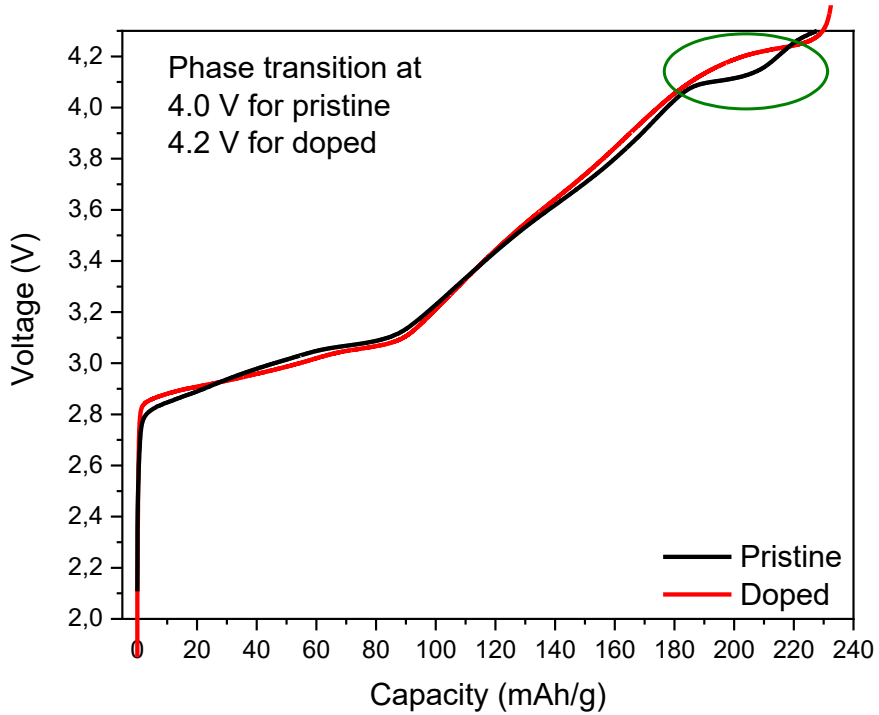
Charge profiles



P3 to O3'' phase transition
at higher voltage in doped material

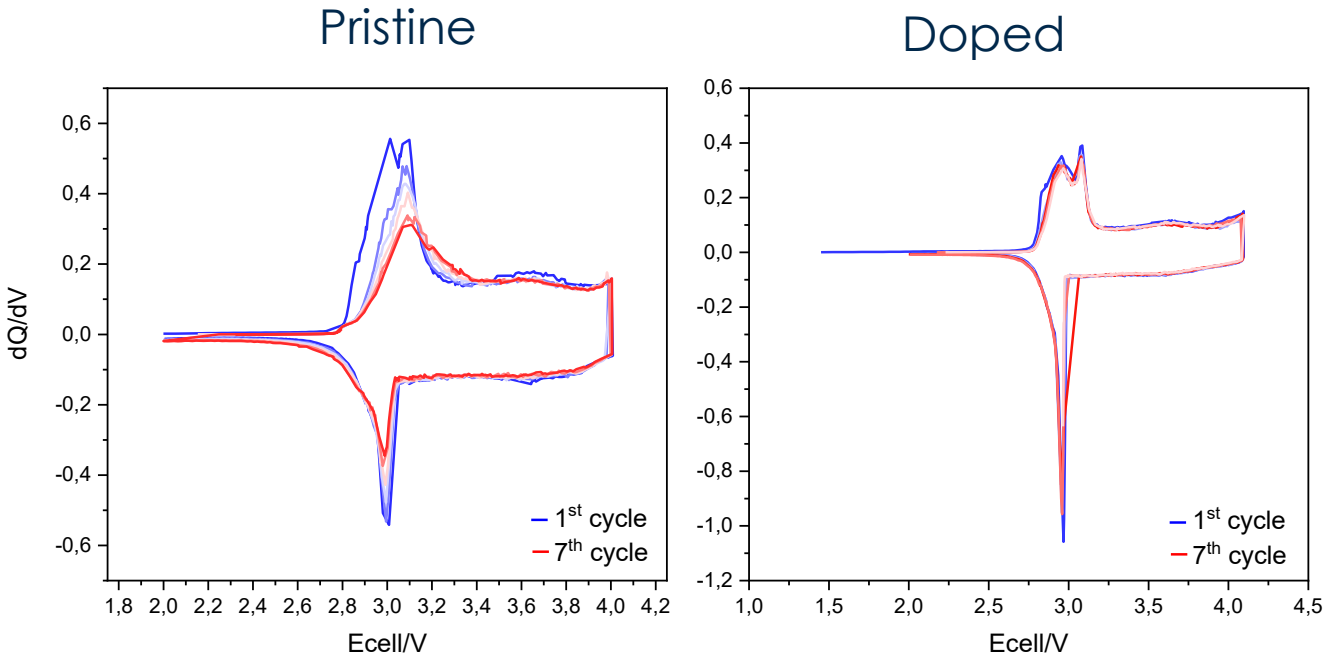
Preliminary electrochemical characterization

Charge profiles



P3 to O3'' phase transition at higher voltage in doped material

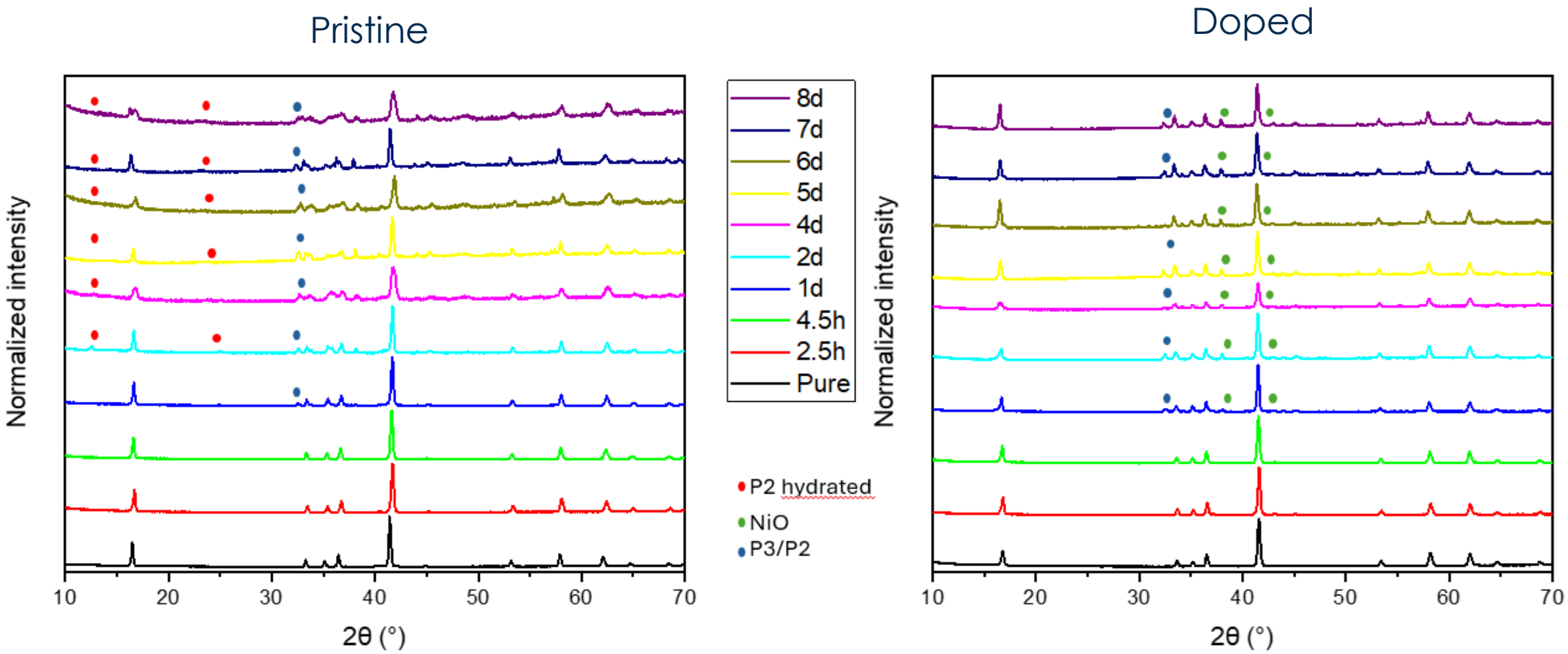
dQ/dV plots



Capacity loss of Fe in pristine material during first cycles

Preliminary moisture sensitivity tests

Material powders exposed to 80% relative humidity at 25 °C in climatic chamber



PXRD patterns collected for 8 days while exposing the samples in the climatic chamber

Conclusion and future perspectives

- Cu doping enhances the structural stability up to 4.2 V
- The doped material better retains its structure upon exposeure to air
- *Operando* XAS and XRD will be employed for understanding the redox activity of transition metals and the reversibility of phase transition

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Thank you!

Group for applied materials and electrochemistry

Preliminary moisture sensitivity tests

Powder exposed to 80% relative humidity at 25 °C: FTIR Spectra