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SORBONNE UNIVERSITÉ

LRS PARIS
Laboratoire de Réactivité de Surface

Study of the negative electrode with ionic liquid electrolyte for a new proton battery concept

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Outline

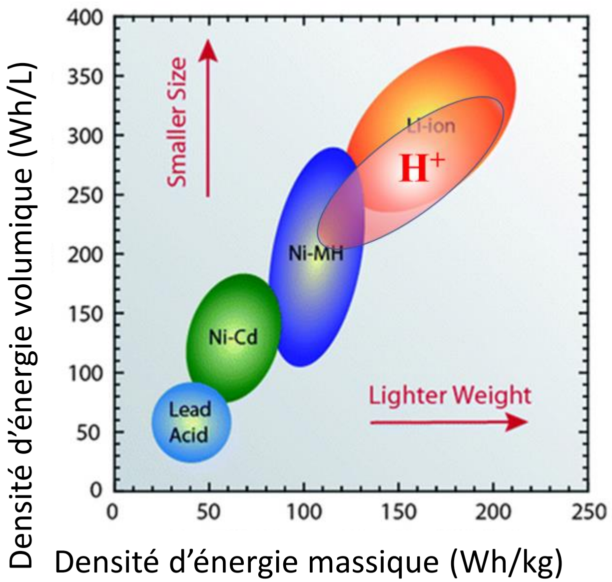
Advantages and limitations of Li-ion and Ni-*M*H batteries

Li-ion

☺
- ✓ High energy density
- ✓ High power

☹
- X Safety: flammable organic electrolyte

➥ WiS electrolytes
➥ Na, Mg batteries



Ni-*M*H

☺
- ✓ Security and Robustness
- ✓ Low-cost

☹
- X Energy density: narrow electrochemical window of water
- X Lifetime : electrode corrosion in KOH solution

➥ **Protonic conducting battery in ionic liquid (IL) electrolyte**:

Charge career: abundant, light-weight, enables a quick ionic conduction

Concept inspired from Ni-*M*H batteries but modifying the electrolyte and the negative and positive electrodes.

Ionic liquids

- Salts that are liquid below 100˚C
- Their physical and chemical properties can be tailored by mixing them with other compounds [1]
- Nonflammable, non-volatile and recyclable

⇨ Safe electrolyte

- Two families: aprotic and protic (PIL)
- PIL = mobile proton with conductivity above 1 mS.cm^{-1} [2]

⇨ Possible application as proton exchange electrolyte

- Wide electrochemical window

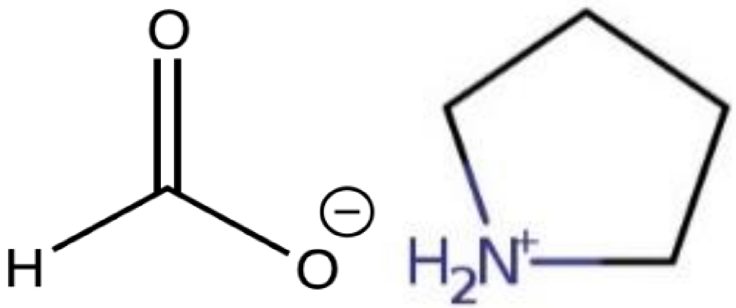
⇨ High cell potential enabling high energy density W = Q x U

capacity (Q) — voltage (U)

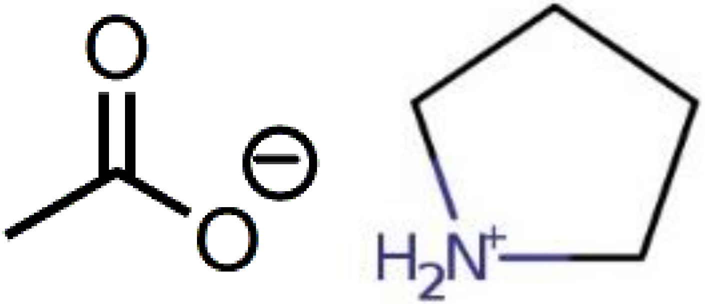
[1] : L. Segade *et al.*, *J. Molecular Liquids*, 2016, **222**, 663

[2] : M. Watanabe *et al.*, *Chemical Reviews*, 2017, **117**, 7190

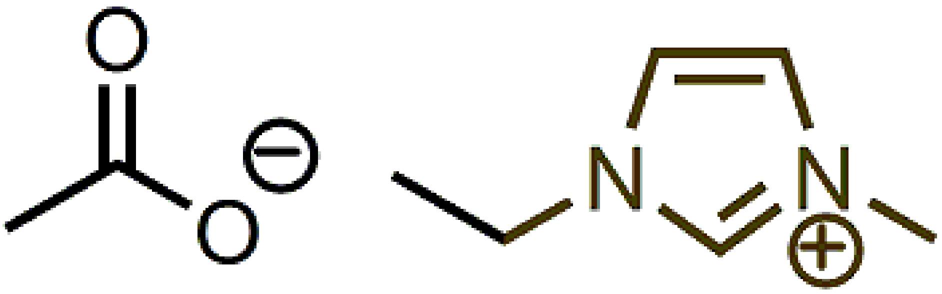
Ionic liquids



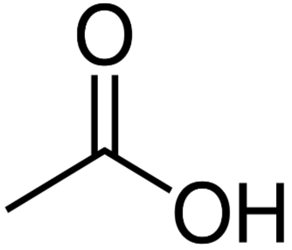
Pyrrolidinium Formate [Pyrr][F]



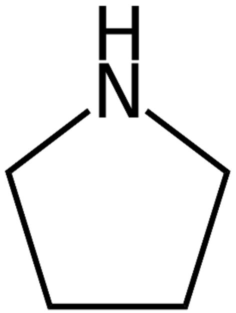
Pyrrolidinium Acetate [Pyrr][Ac]



1-ethyl-3-methylimidazolium acetate
[EMIM][Ac]



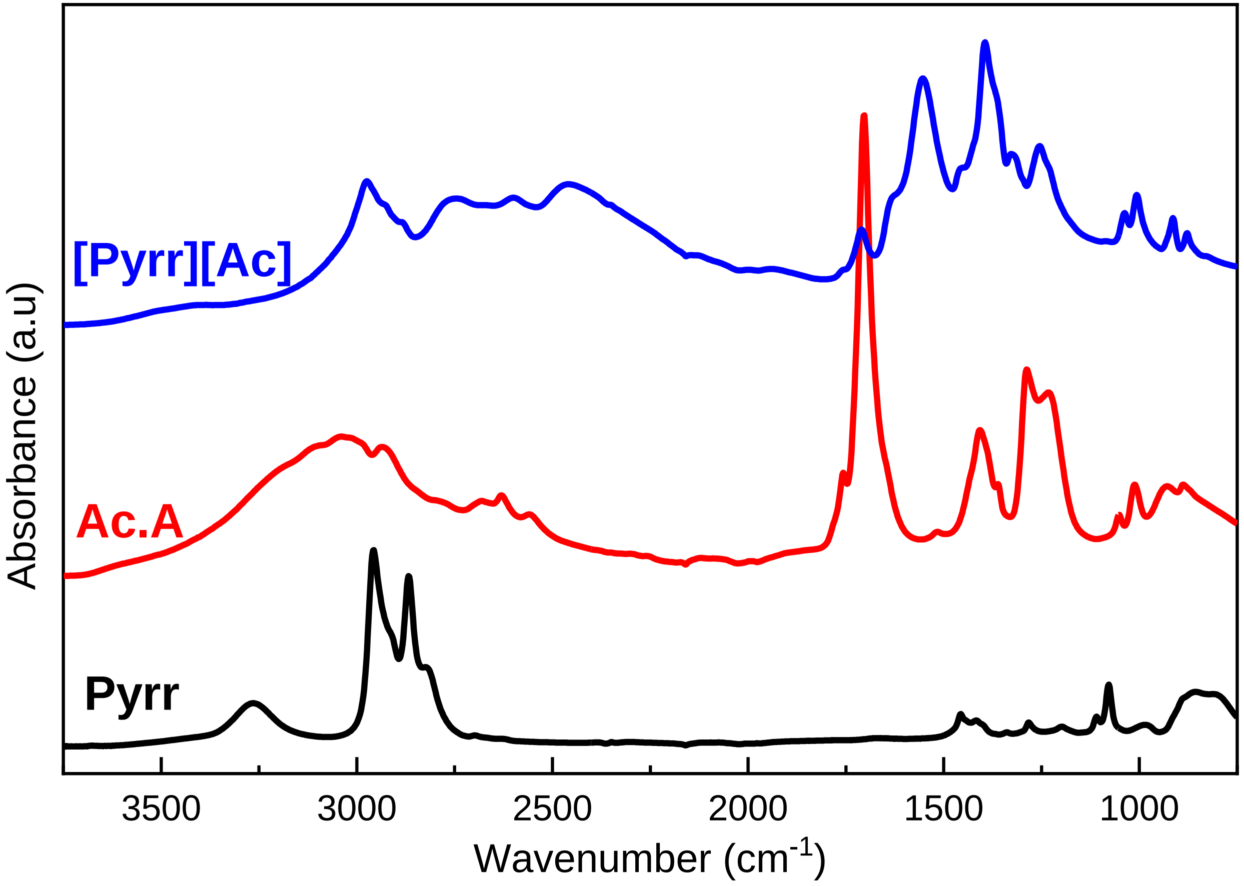
Acetic Acid



Pyrrolidine

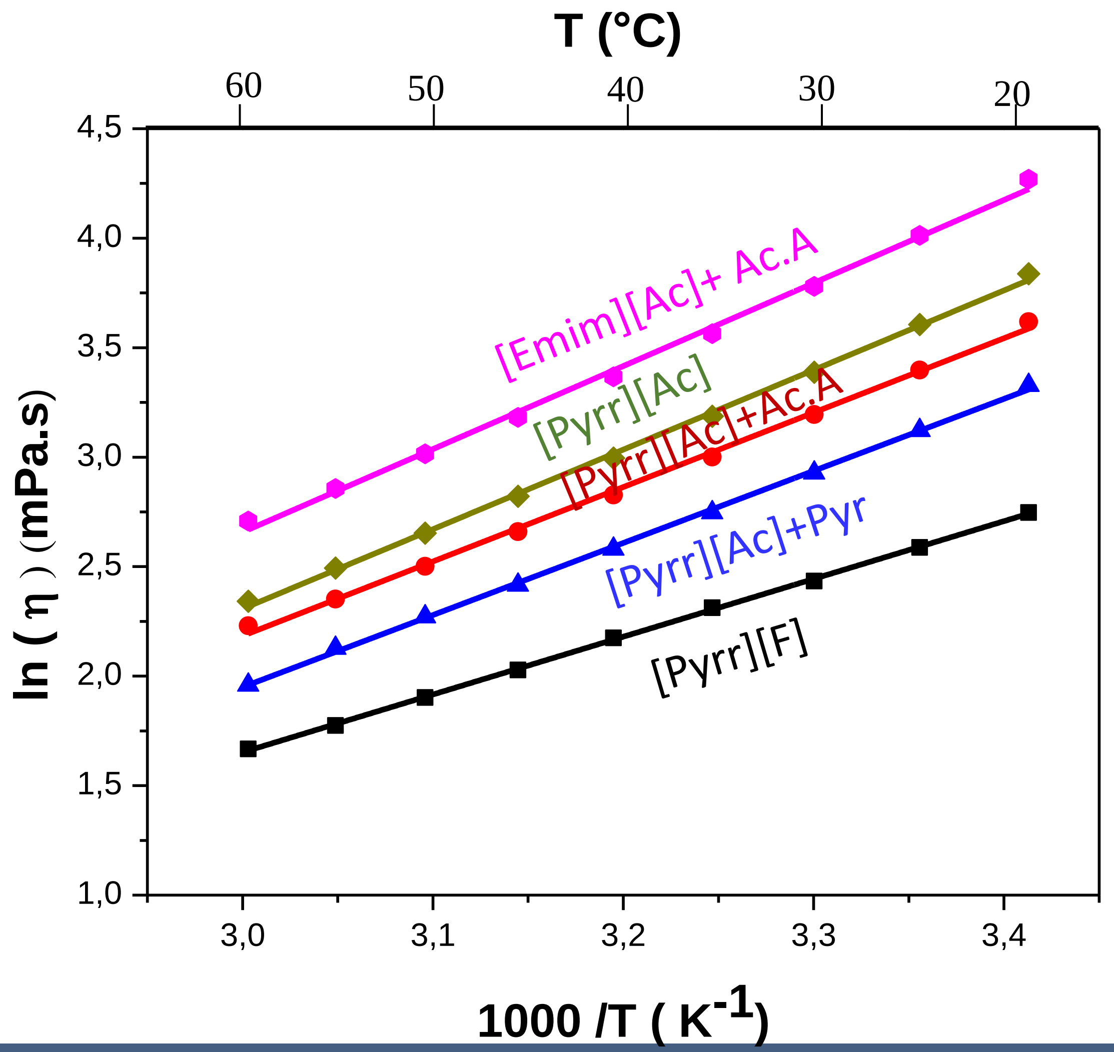
Ionic liquids: synthesis

- FTIR of synthesized [Pyrr][Ac] in comparison with Ac.A and Pyrr

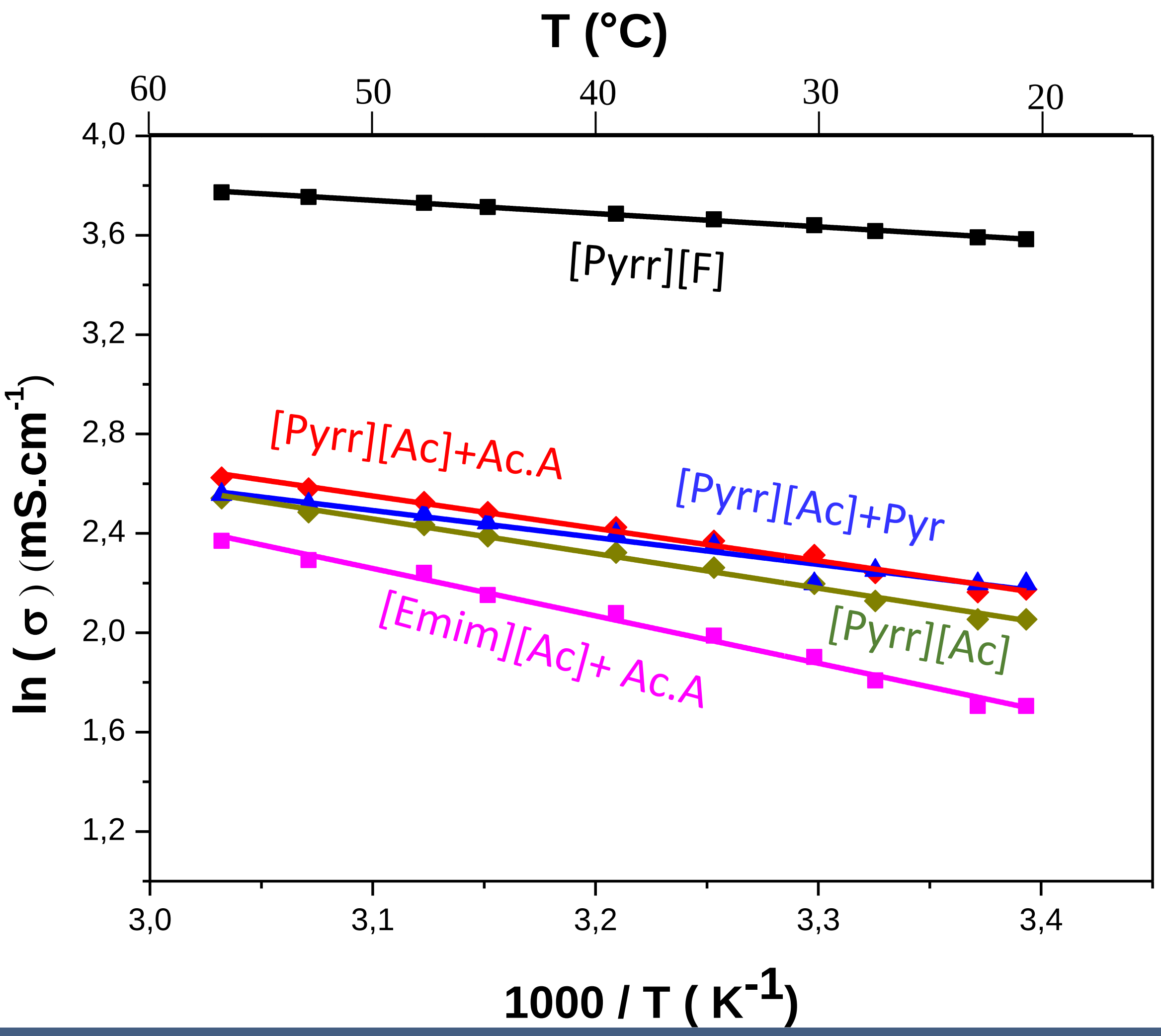


Ionic liquids: physico-chemical properties

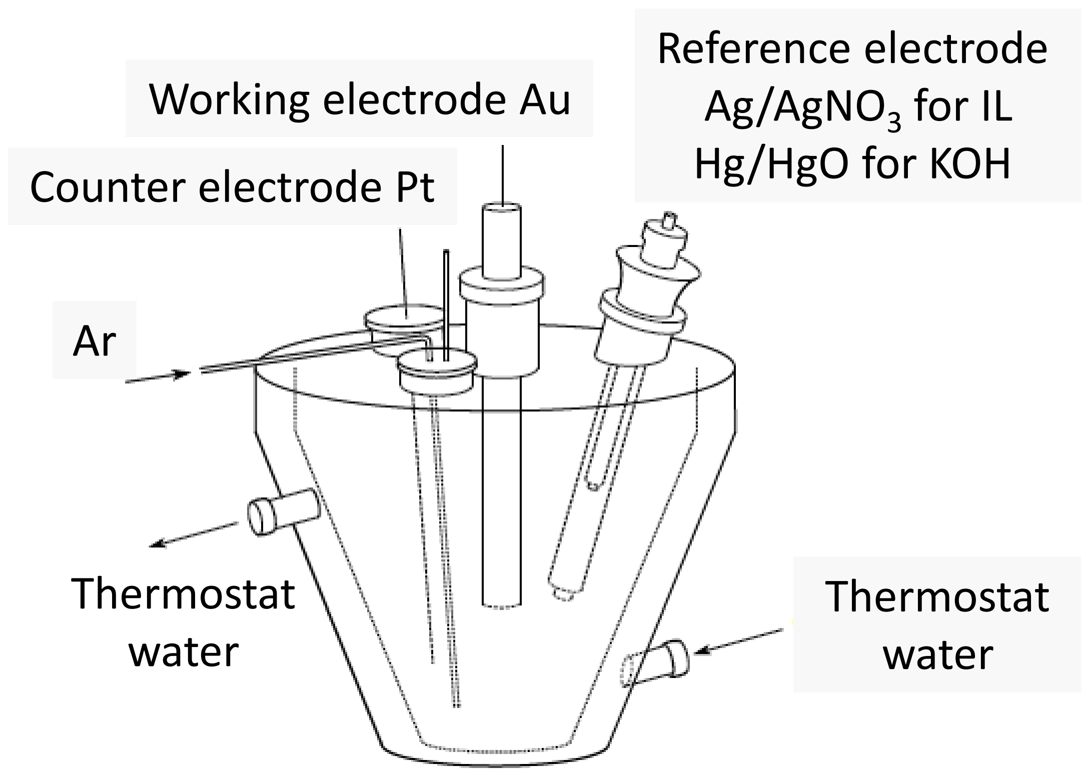
Dynamic viscosity *vs* temperature



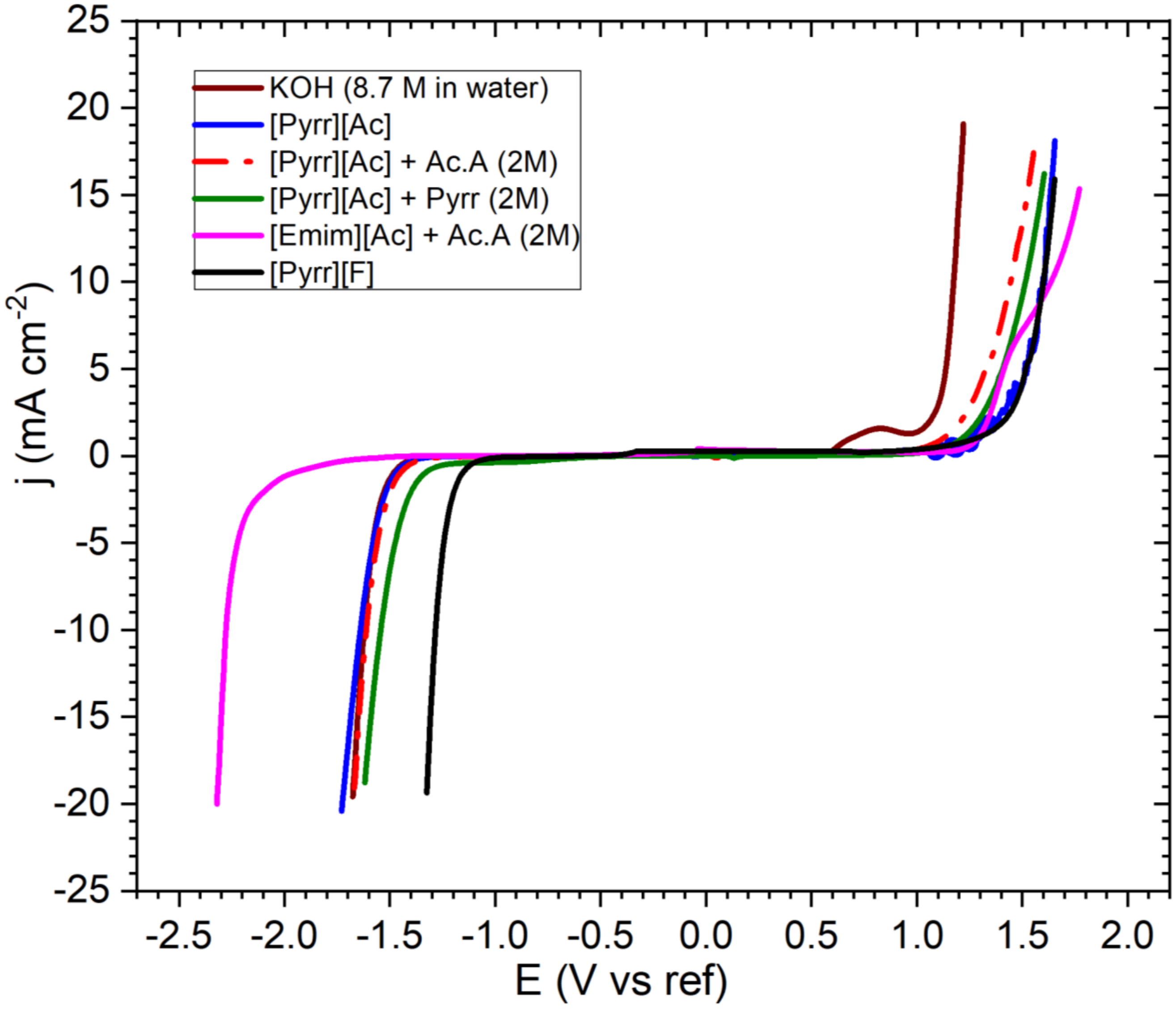
Ionic conductivity *vs* temperature



Ionic liquids: electrochemical window



3-electrode electrochemical Cell
Linear sweep voltametry, 5 $mV.s^{-1}$



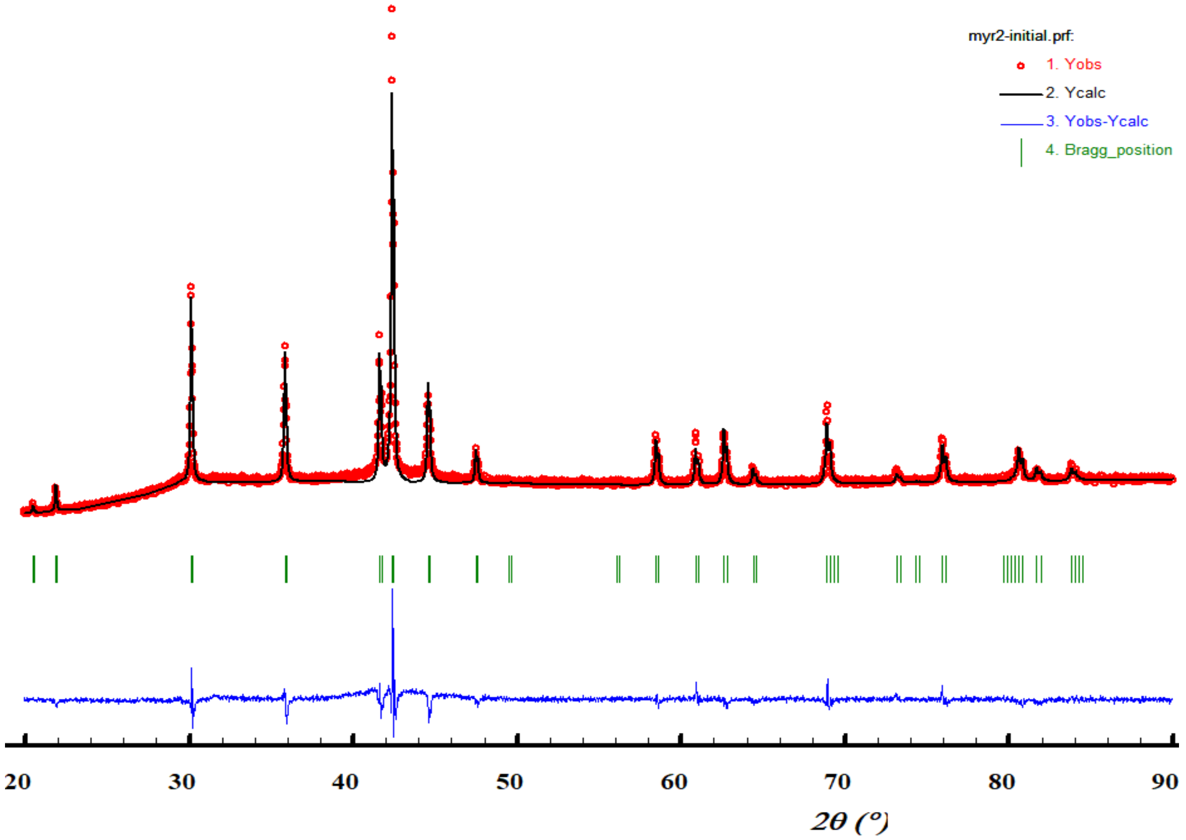
Ionic liquids: summary

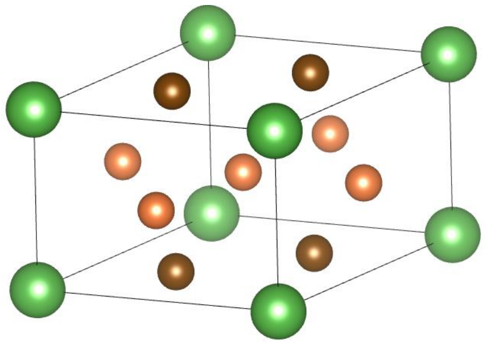
Medium	η at 25°C (mPa.s)	E_η (kJ. mol^{-1})	σ at 25°C (mS. cm^{-1})	E_σ (kJ. mol^{-1})	E_{window} (V)
[Pyrr][F]	12.5	21.92	36.63	4.42	2.0
[Pyrr][Ac]	34.1	30.21	9.20	11.58	2.2
[Pyrr][Ac] + Ac (2M)	28.0	28.24	8.04	10.85	2.3
[Pyrr][Ac] + pyr (2M)	21.1	27.34	8.96	9.03	2.4
[EMIM][Ac]+Ac(2M)	50.9	31.51	5.72	15.85	3.0

- The medium with low viscosity provides high conductivity!
- Electrochemical window wider than that of KOH aqueous solution

Half cell test: working electrode

Active material: AB_5 –type alloy





a = 5.0086 Å
c = 4.0026 Å

S.G. $P6/mmm$

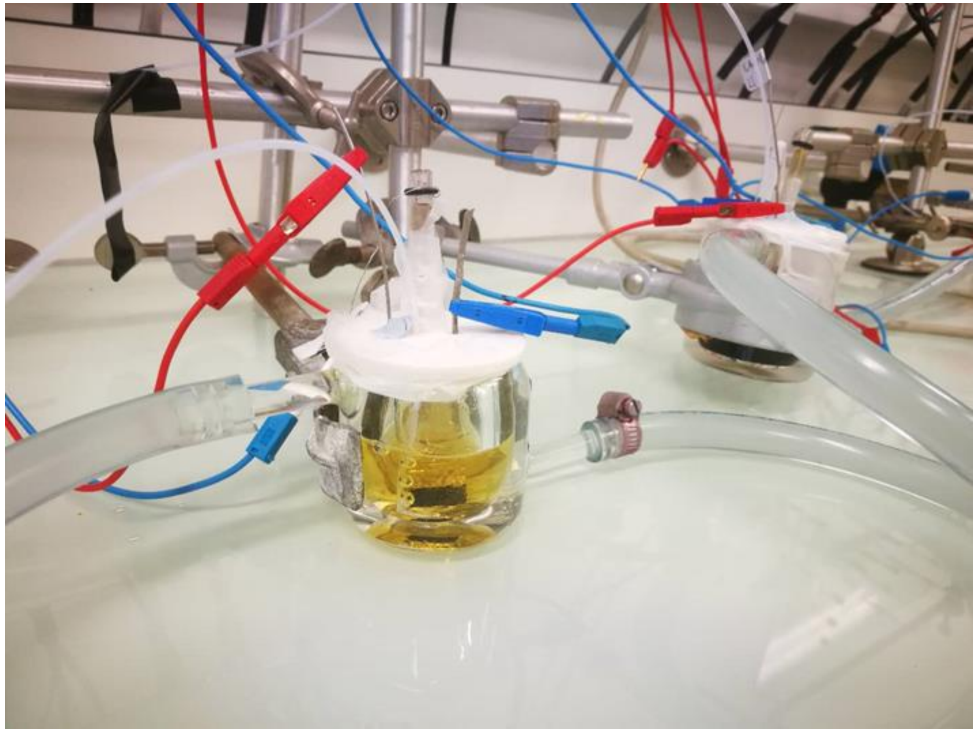
Composite electrode formulation:

- 90 wt. % alloy (active material)
- 5 wt. % carbon black (conductor)
- 5 wt. % PTFE (binder)

Half cell test: galvanostatic cycling

3-electrode electrochemical cell:

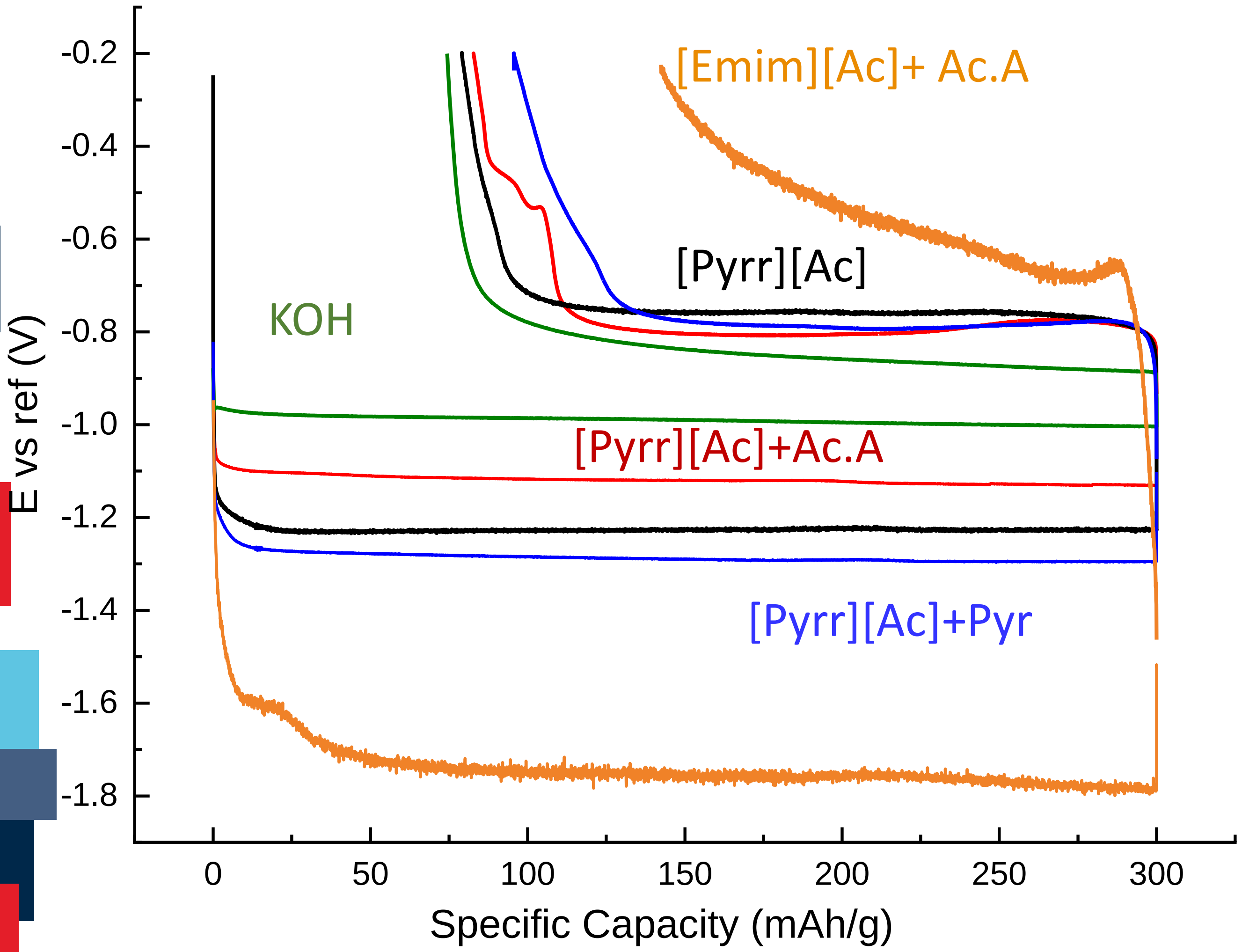
- **Working electrode: composite *AB_5*** pressed on a Ni-grid
- **Reference electrode:** Hg/HgO for KOH solution, Ag/$AgNO_3$for ILs
- **Counter electrode:** Platinum grid

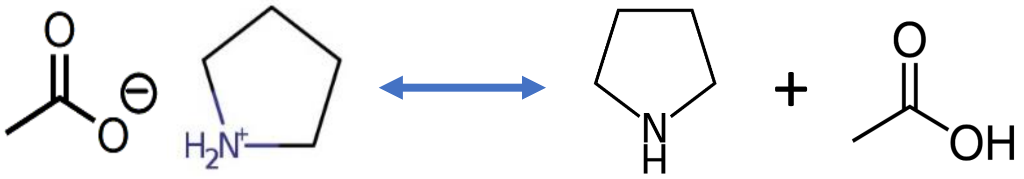


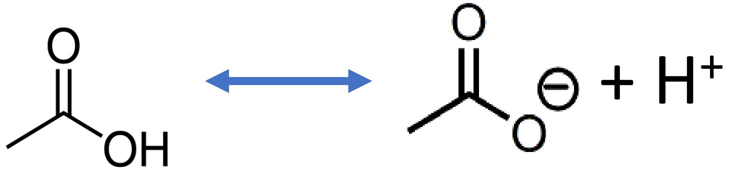
Galvanostatic cycling regime:

- C/40 for ILs
- C/10 for KOH solution

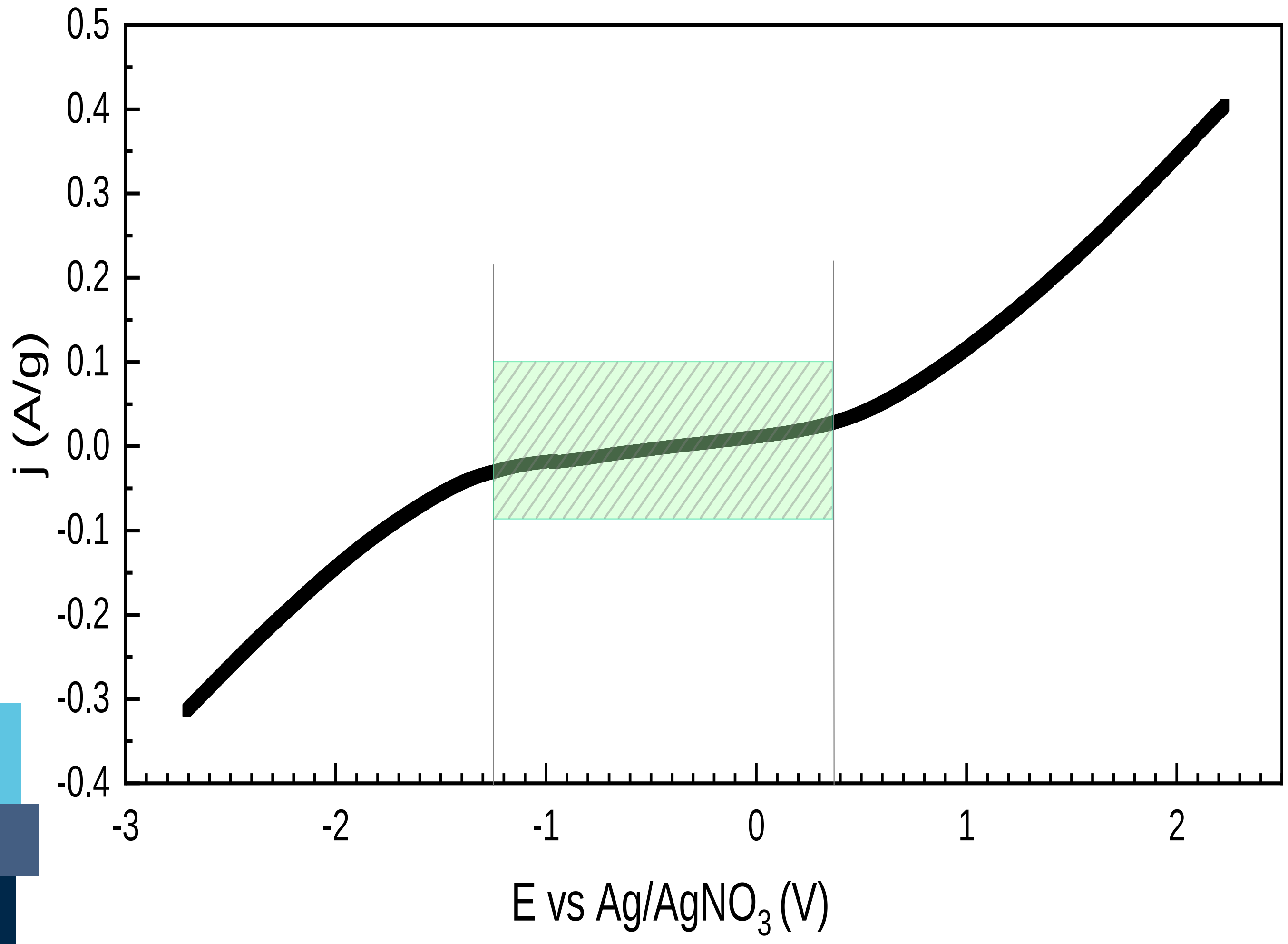
Half cell test: galvanostatic cycling

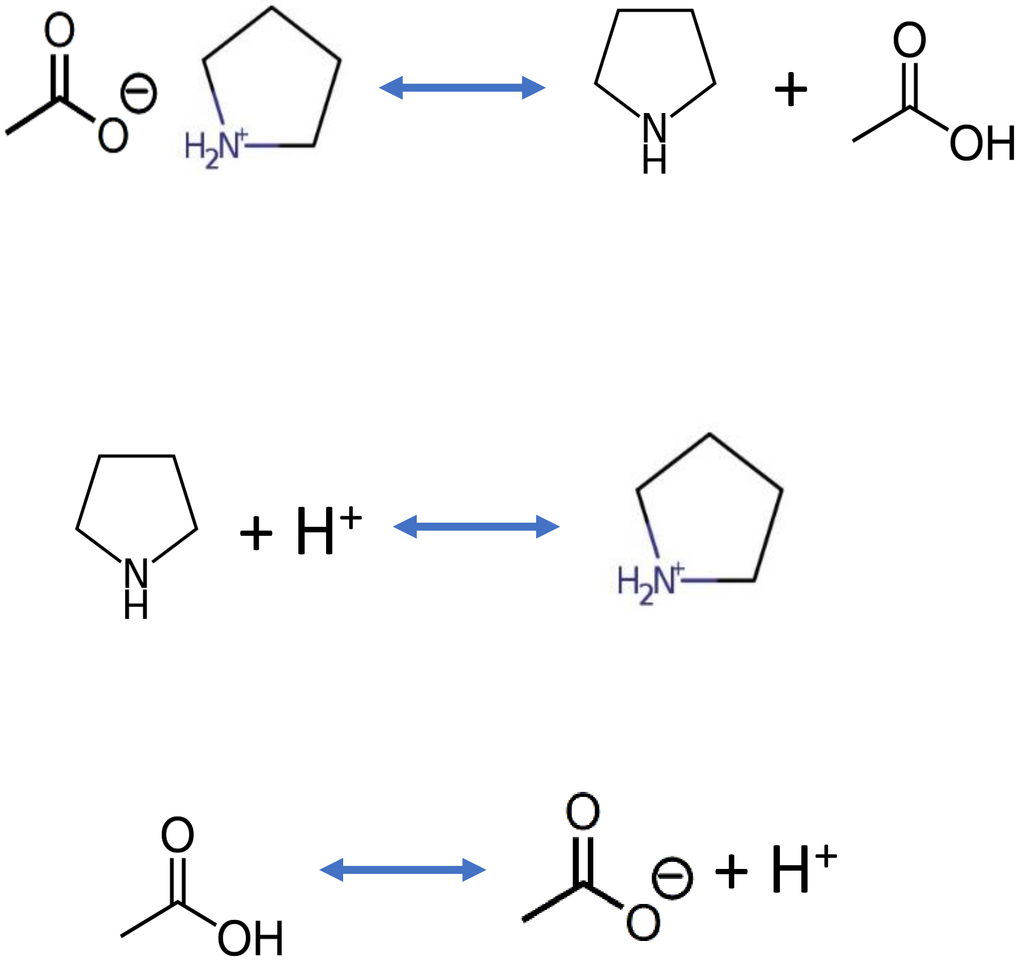




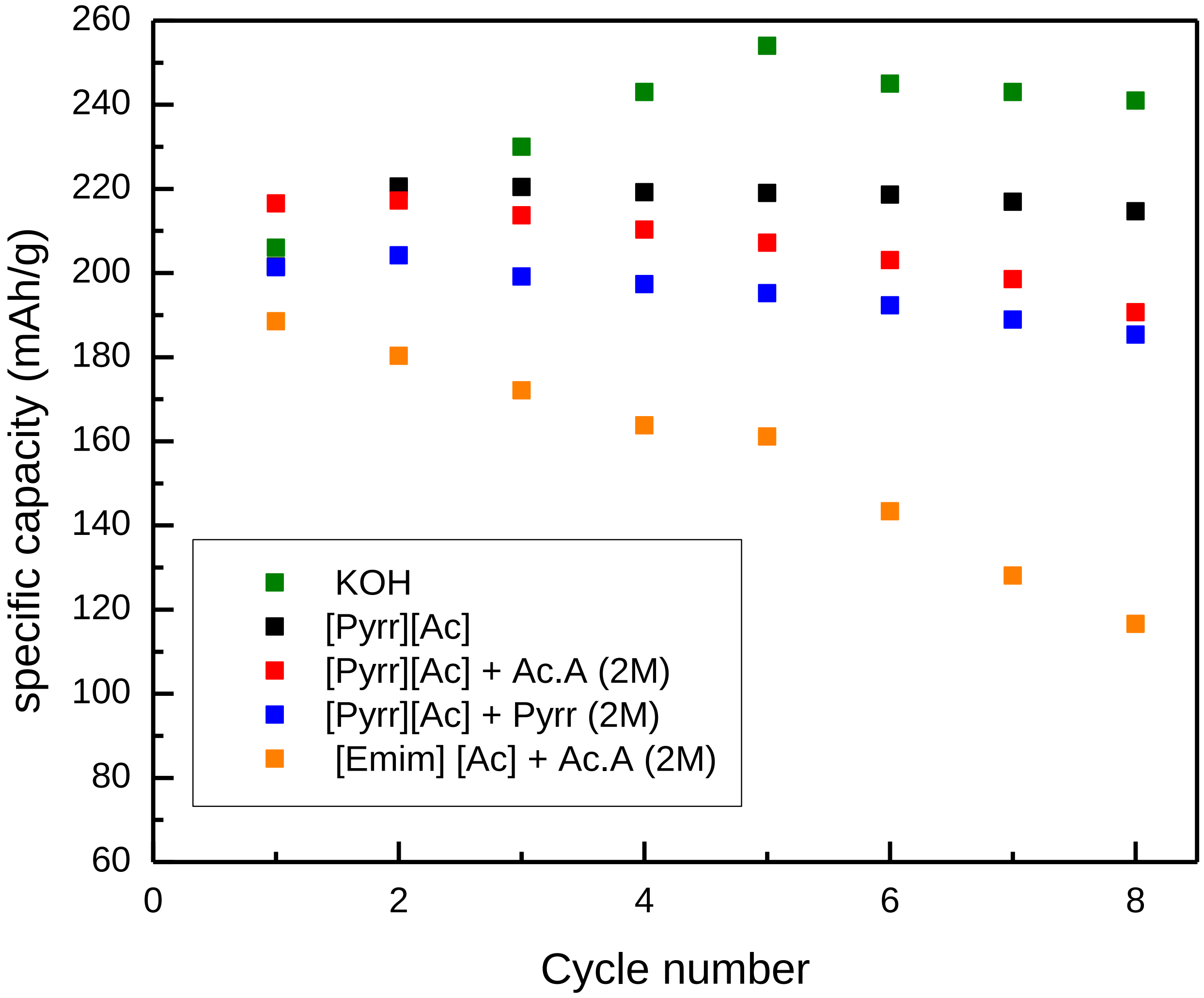


Half cell test: galvanostatic cycling





Half cell test: galvanostatic cycling



Capacity *vs* cycle number:

- The highest capacity is obtained in KOH medium after activation cycles
- For Ils, capacity increases as [Pyrr][Ac]+Pyr < [Pyrr][Ac]+Ac.A < [Pyrr][Ac]
- The lowest capacity is observed for [Emim][Ac]+ Ac.A, and it decreases rapidly
- [Pyrr][Ac] shows the best properties. It will be further investigated

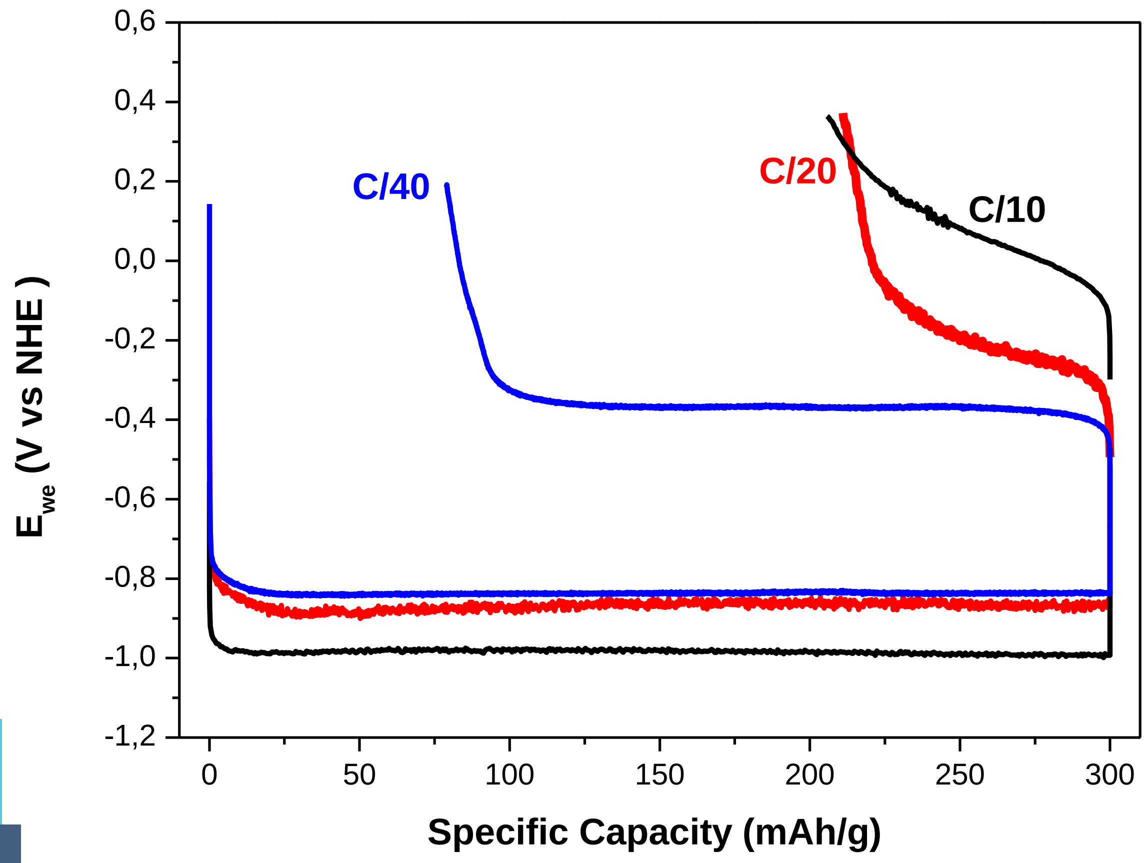
Half cell test: galvanostatic cycling

Medium	1st cycle capacity ($mAh.g^{-1}$)	Maximum capacity ($mAh.g^{-1}$)	8th cycle's capacity ($mAh.g^{-1}$)	Capacity decrease
KOH	206	254	229	10 %
[Pyrr][Ac]	202	221	215	3%
[Pyrr][Ac] + Ac.A. (2M)	217	217	191	12 %
[Pyrr][Ac] + Pyrr (2M)	201	204	185	9 %
[EMIM][Ac] +Ac(2M)	189	189	117	38 %

Maximum capacity and capacity decrease:

- The highest capacity is obtained in KOH medium after activation cycles
- For Ils, capacity increases as [Pyrr][Ac]+Pyr < [Pyrr][Ac]+Ac.A < [Pyrr][Ac]
- The lowest capacity is observed for [Emim][Ac]+ Ac.A, and it decreases rapidly
- [Pyrr][Ac] shows the best properties. It will be further investigated

Half cell test: galvanostatic cycling

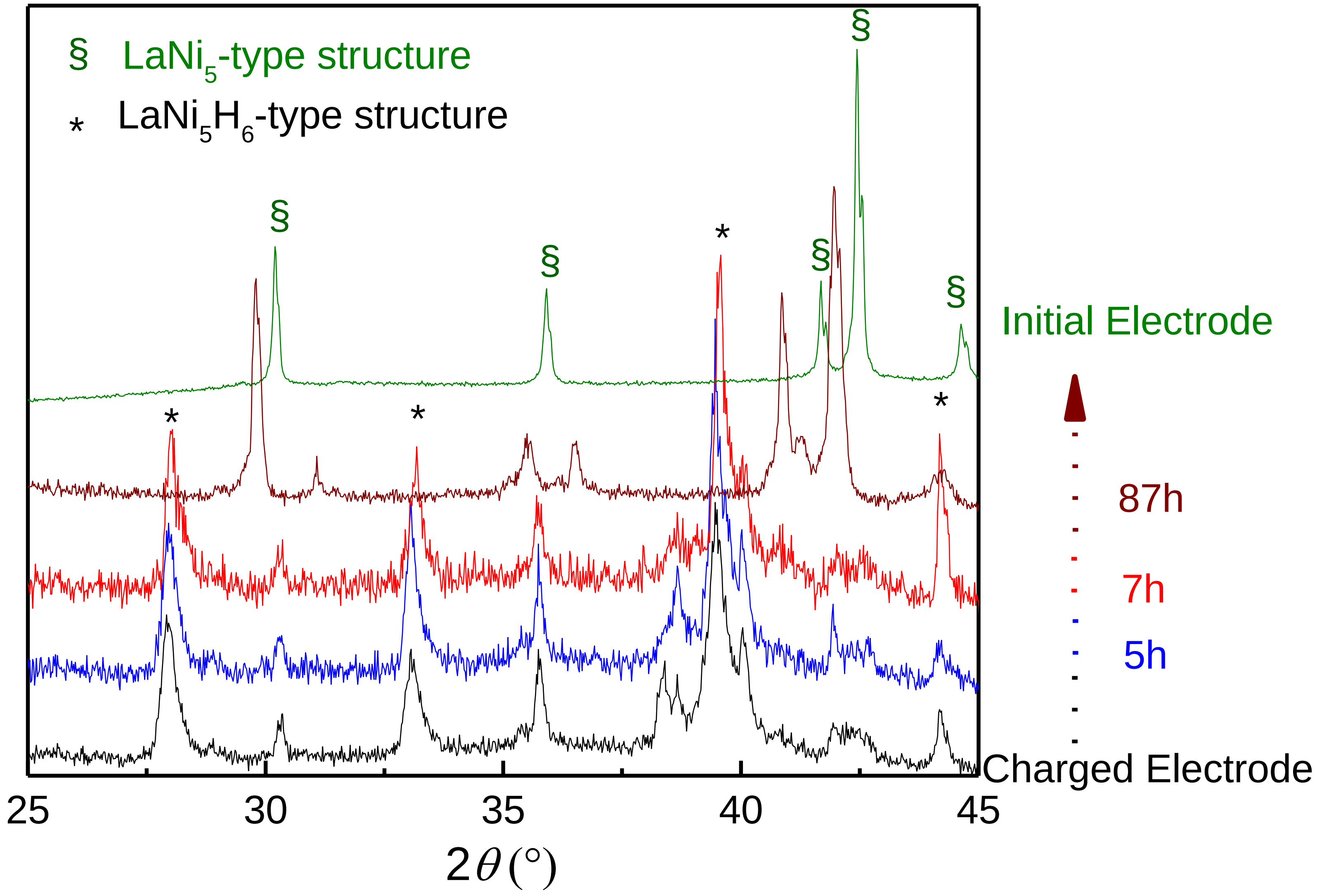


AB_5 in [Pyrr][Ac] at different C-rates:

- Charge potential changes little
- Discharge potential strongly increases with C-rate
- Reversible capacity decreases with C-rate

- Kinetic limitation of charge transport?

XRD of electrode after charge: evidence of hydrogen transfer



- XRD of the charged electrode containing the AB_5H_6 hydride phase
- *M*H releases some hydrogen spontaneously
- *M*H amount decreases with measuring time and finally convert into the intermetallic *M* phase

Conclusions and prospects

- [Pyrr][F] and [Pyrr][Ac] have been synthesized, their mixtures with acetic acid and pyrrolidine have been studied as electrolytes for proton exchange batteries.
- An AB_5-type alloy has been cycled with ILs. A specific capacity of 216 mAh·g^{-1} was obtained in [Pyrr][Ac]
- Obtained results are promising with a capacity close to that obtained in KOH medium
- The XRD of the charged electrode confirms that electrochemical cycling leads to the hydrogenation and dehydrogenation of the intermetallic compound.
- Further question may be raised for the electrolyte, the electrode/electrolyte interface.
- Positive side: to be explored

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Thank you for your kind attention!

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