Bromine complexation agents in H_2/Br_2 flow battery cathodes: Physicochemical processes and their influence on cell operation and cell performance

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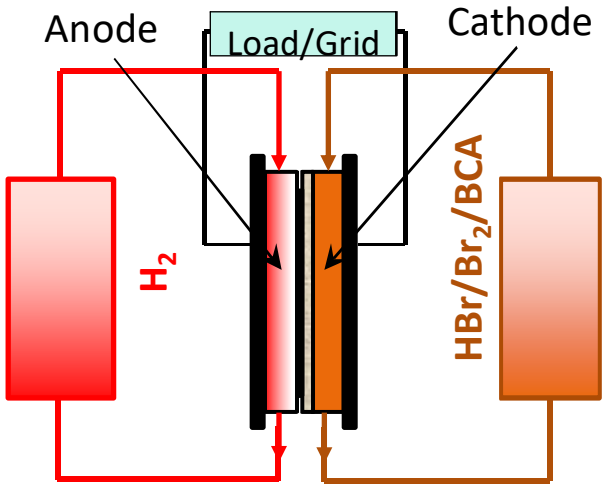
Motivation for Cathodes in H_2/Br_2 RFB

- Fast reaction kinetics at anode and cathode
- Energy density up 225 Wh L^{-1} (6.7 M HBr)
- Bromine catholyte: reactand = electrolyte



OCV: $E_{OCV} = 1.09\ V$

Bromine storage as polybromide:

Catholyte: $Br_2 + Br^- \rightleftharpoons Br_3^-$

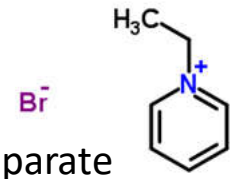
Catholyte: $xBr_2 + Br^- \rightleftharpoons Br_{1+2x}^-$

Challange of bromine cathode:

Volatility, Toxicity

Extraction of bromine:
Quarternary ammonium cations

Capture bromine in a separate phase



Ethylpyridiniumbromide: C_2PyBr

SOC 0: 7.7 M HBr and 1.11 M C_2PyBr

SOC 100: 1 M HBr; 3.35 M Br_2 and 1.11 M C_2PyBr

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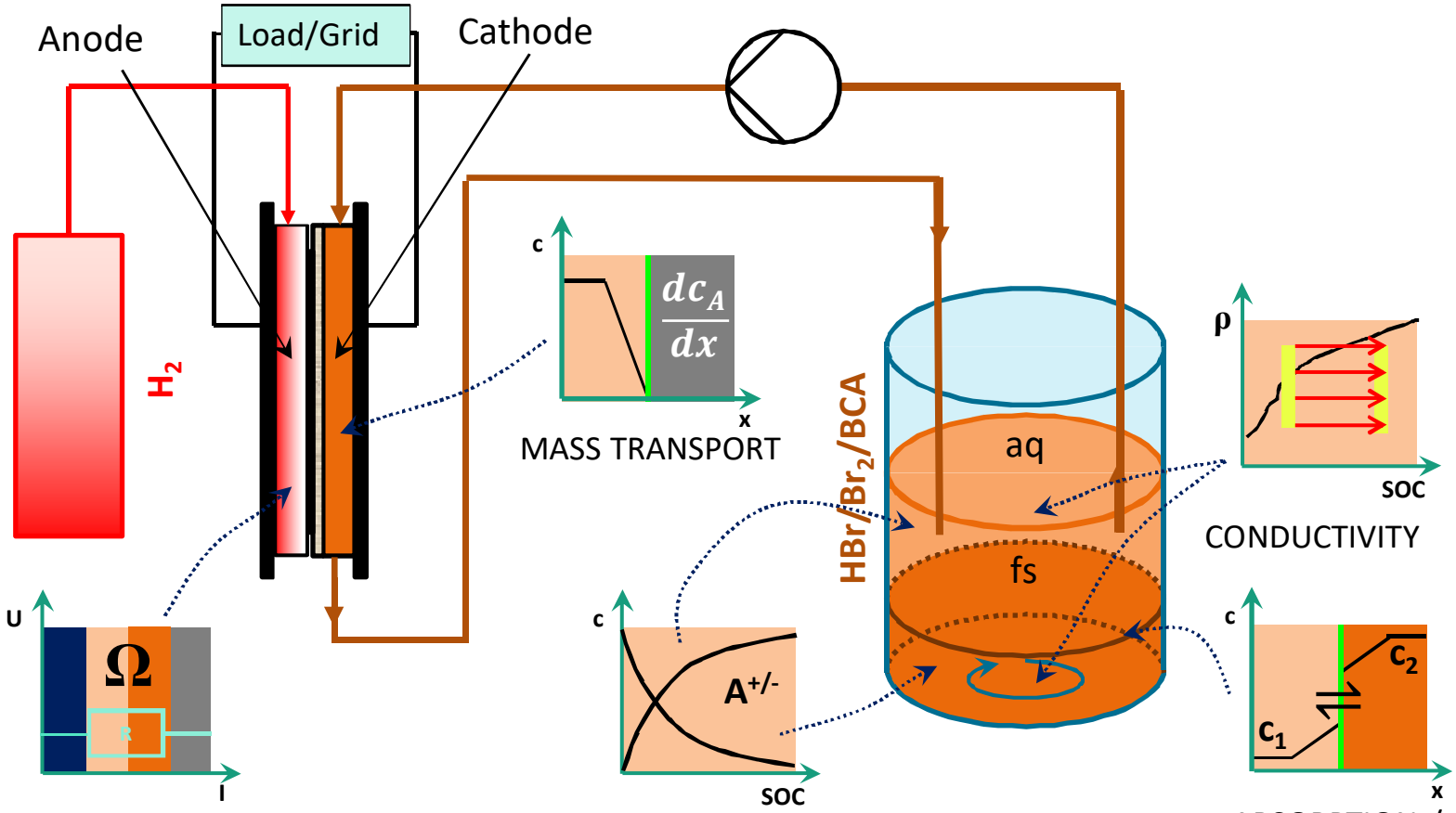
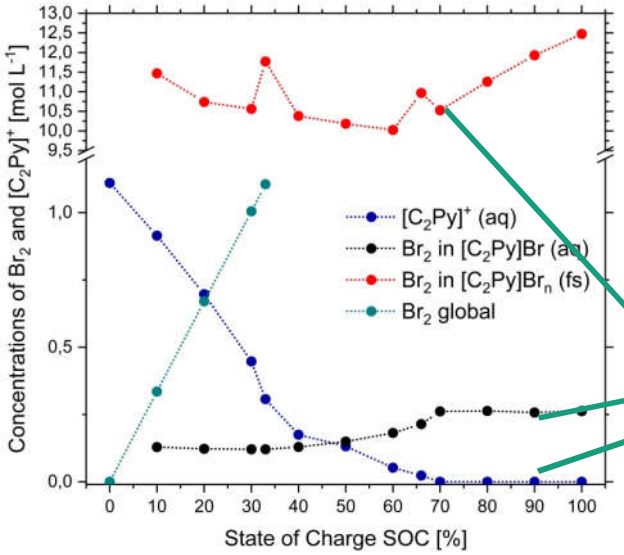
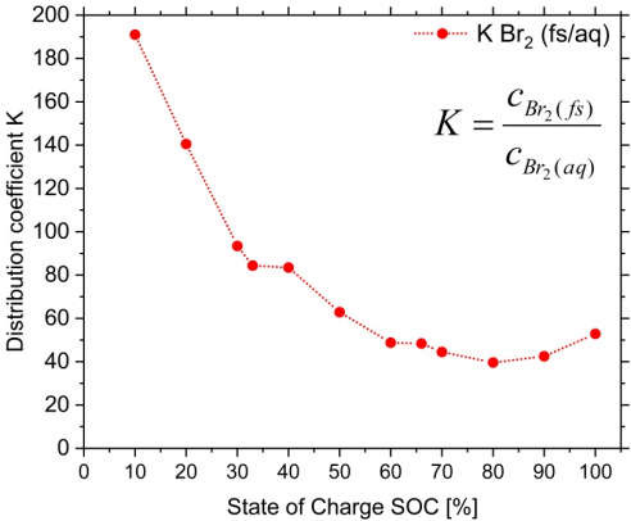
Influences of $[C_2Py]Br$ on cell perf. at various SOC ?



How strong is Br_2 bound to $[C_2Py]^+$?



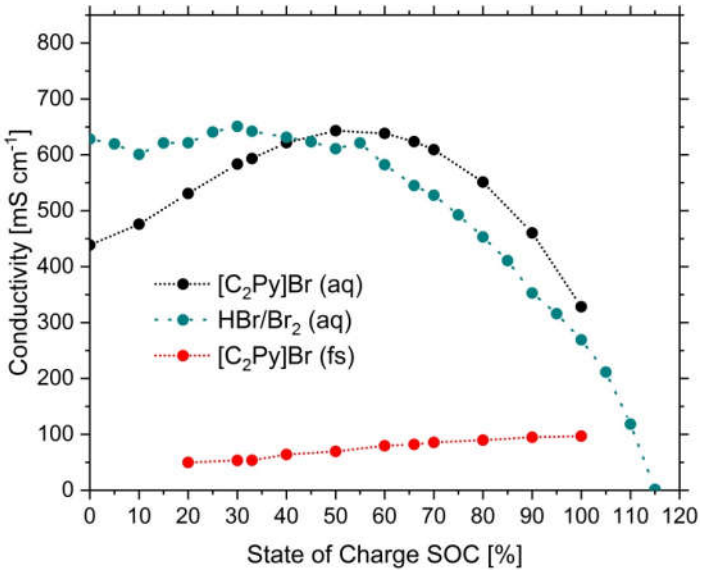


- Bromine concentration in fused salt around 11 M Br_2 >>> 640 Wh L^{-1}
- Strong complexation of Br_2 with $[C_2Py]^+$ … 0.35 M Br_2 vs. 3.35 M Br_2 at SOC 100 – leading to a safer catholyte

$$BCA^+(aq) + Br^-(aq) + xBr_2(aq) \rightleftharpoons \boldsymbol{BCABr_{2x+1}(fs)}$$

- Complexation of Br_2 with $C2Py^+$ leads to falling $C2Py^+$ concentration in aqueous phase

Conductivity of catholyte aq + fs



- Fused salt phase showing conductivities between 45 and 90 mS cm^{-1}

- Conductivities of pure $HBr/Br_2/H_2O$ phase at around 625 mS cm^{-1} for SOC 0 to SOC 50 and falling for SOC > 60. The proton amount in the electrolyte falls due to cell reaction.
- C_2Py^+ limits the conductivity in accordance to concentration plot (445 mS cm^{-1})
- Complexation of C_2Py^+ with Br_2 and extraction of fused salt leads to rising conductivities for SOC 0 (445 mS cm^{-1}) to SOC 60 (643 mS cm^{-1})

Bromine extraction:

$$BCA^+(aq) + Br^-(aq) + xBr_2(aq) \rightleftharpoons BCABr_{2x+1}(fs)$$

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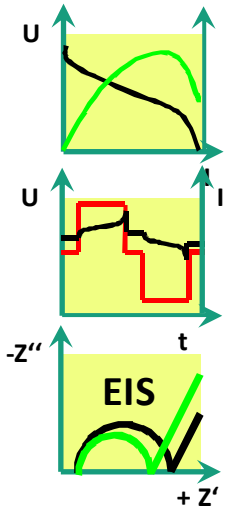
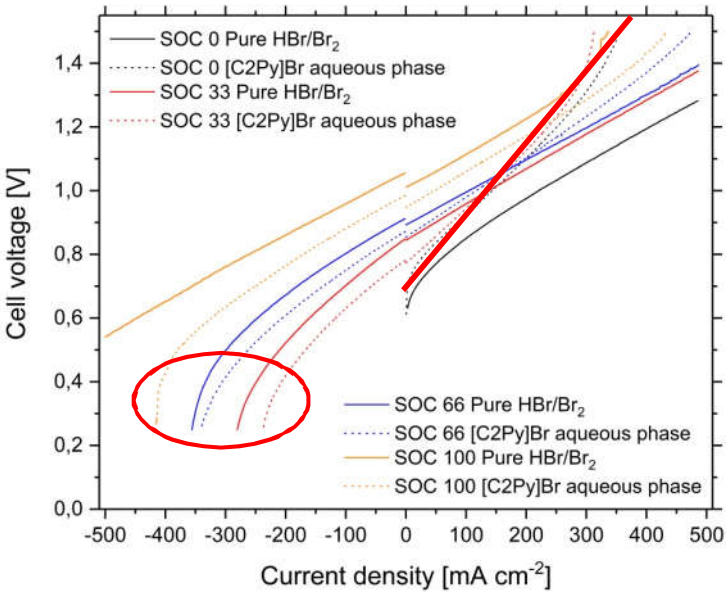
H_2/Br_2 RFB – Celltest with C_2Py^+

- Bromine cathode - aqueous phase pumped around
  - Graphite felt (GFA 5, SGL, Carbon, D)
  - Current collector Glassy Carbon (Sigradur G, HTW, D)
- Hydrogen anode / MEA– 40 cm² active area (membrane)
  - Nafion 117®, 3 mg Pt cm^{-2} on carbon cm² surface) + GDL (BC 25, SGL Carbon, D)
  - 100 mL min^{-1} H_2 flow (nonrecyclable)



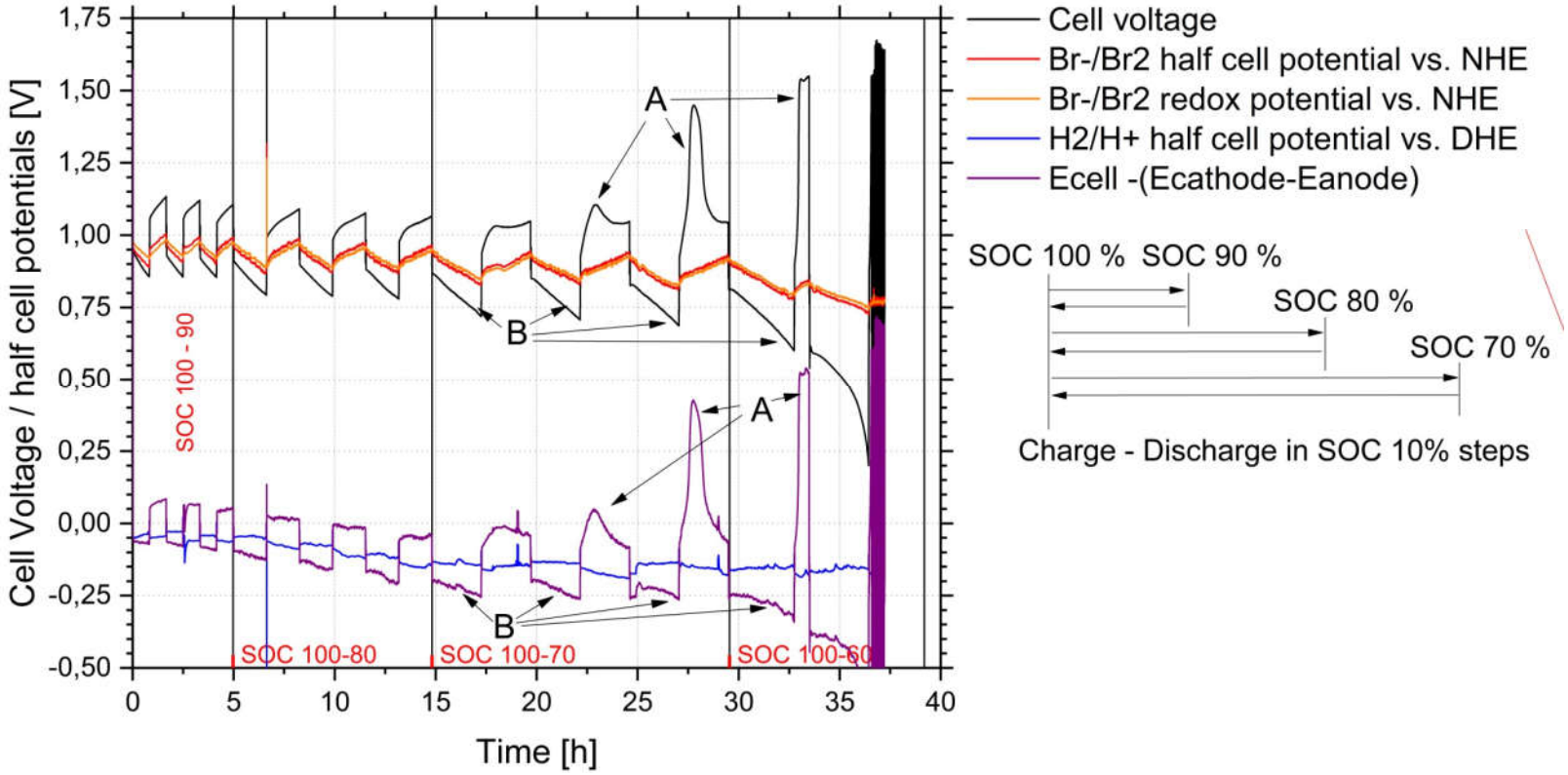
- Linear sweep potentiometry: +/- 1.25 mA cm^{-2} s^{-1} in the range of 0 to 500 mA cm^{-2} – threshold points: 0.25 V and 1.5 V
- Galvanostatic cycling test +/- 50 mA cm^{-2}; threshold points: 0.25 V and 1.5 V including detection of half cell potentials and redox potential of the catholyte
- Ohmic cell resistances by galvanostatic electrochemical impedance spectroscopy (EIS) - Amplitude: +/- 10 mA cm^{-2}

Linear sweep potentiometry with C_2Py^+ and without



- Discharge LSP limited by mass transport limitation: $c(Br_2)$ lower for C_2Py^+
- Charge LSP with high ohmic resistances for SOC 0 % (2.2 Ohm cm²) and SOC 33 % (2.4 Ohm cm²), compared to SOC 66 % (0.93 Ohm cm²) and SOC 100 % (0.81 Ohm cm²).

H_2/Br_2 RFB – Celltest with C_2Py^+



- Rising overvoltage during discharge operation for SOC < 80
- Overvoltage peak during charge process (time dependent)
- Neither anodic potential nor cathodic potential follow these trends

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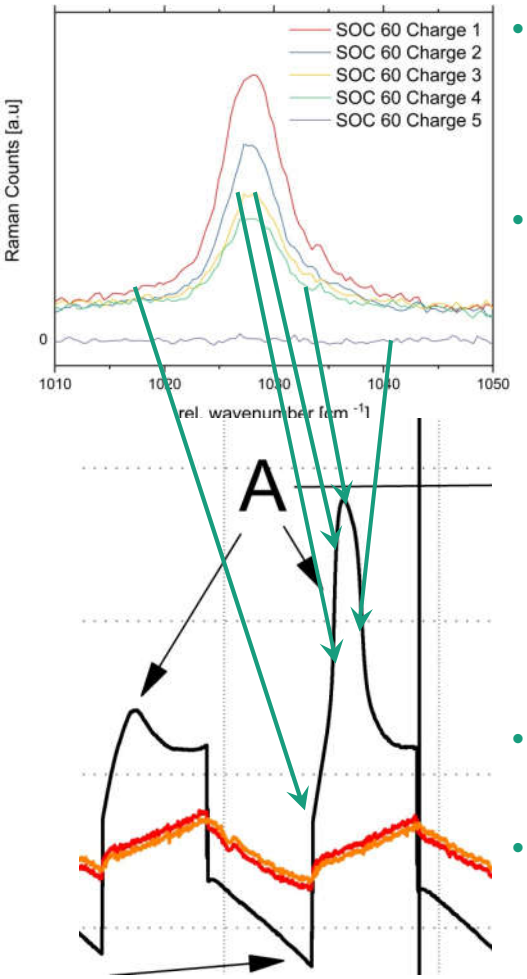
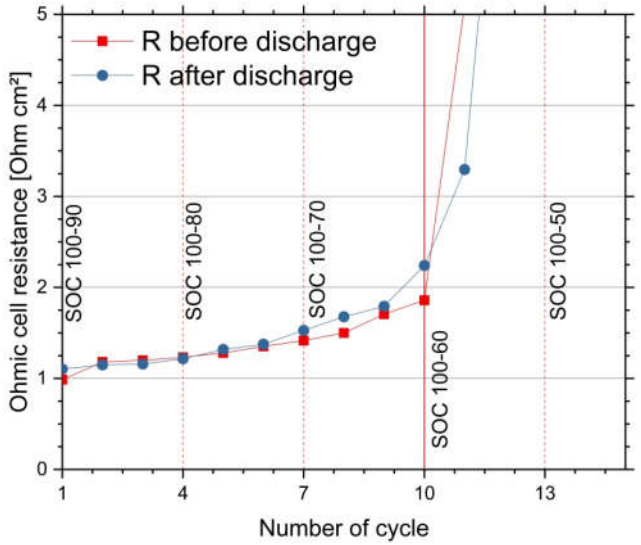
Influence of C_2Py^+ cations on cell performance



- During discharge C_2Py^+ is released from fused salt

$$\boldsymbol{BCABr_{2x+1}(fs)} \rightleftharpoons BCA^+(aq) + Br^-(aq) + xBr_2(aq)$$

- Released C_2Py^+ interacts with PFSA membrane, to lower membrane conductivity



- During charge C_2Py^+ concentration is falling, while an ohmic overvoltage is seen.
- Drops of fused salt flow out of cell outlet >> formation of fused salt in cell reduce conductivity

$$BCA^+(aq) + Br^-(aq) + xBr_2(aq) \rightleftharpoons \boldsymbol{BCABr_{2x+1}(fs)}$$

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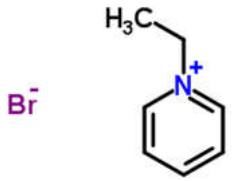
Conclusion

SAFETY



Reducing vapor pressure of bromine in catholyte!

- Composition of electrolyte acts as an important parameter on the performance for the investigated H_2/Br_2 single cell

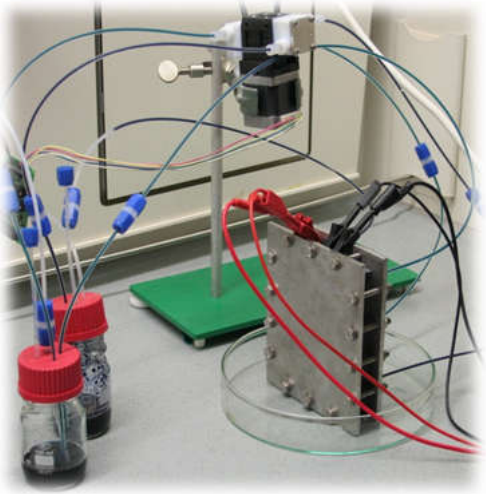
HIGH C_2Py^+ concentrations in aqueous phase lead to

- Decrease of conductivity
- Rising membrane resistance
- Formation of fused salt in cathode (lower conductivity)
- Limiting range of usable SOC to 30%

Got information about processes in cell limiting the PERFORMANCE

Different operation modes and electrolyte formulations shall limit the influence of C_2Py^+, while offering a safe catholyte

THANK YOU FOR YOUR ATTENTION !!



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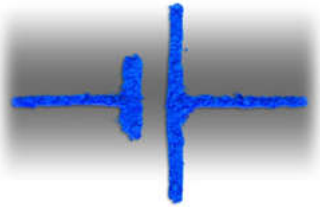

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