Optimizing Membrane Selection and Operational Strategies for Scalable Zinc-Iodine Hybrid Flow Batteries

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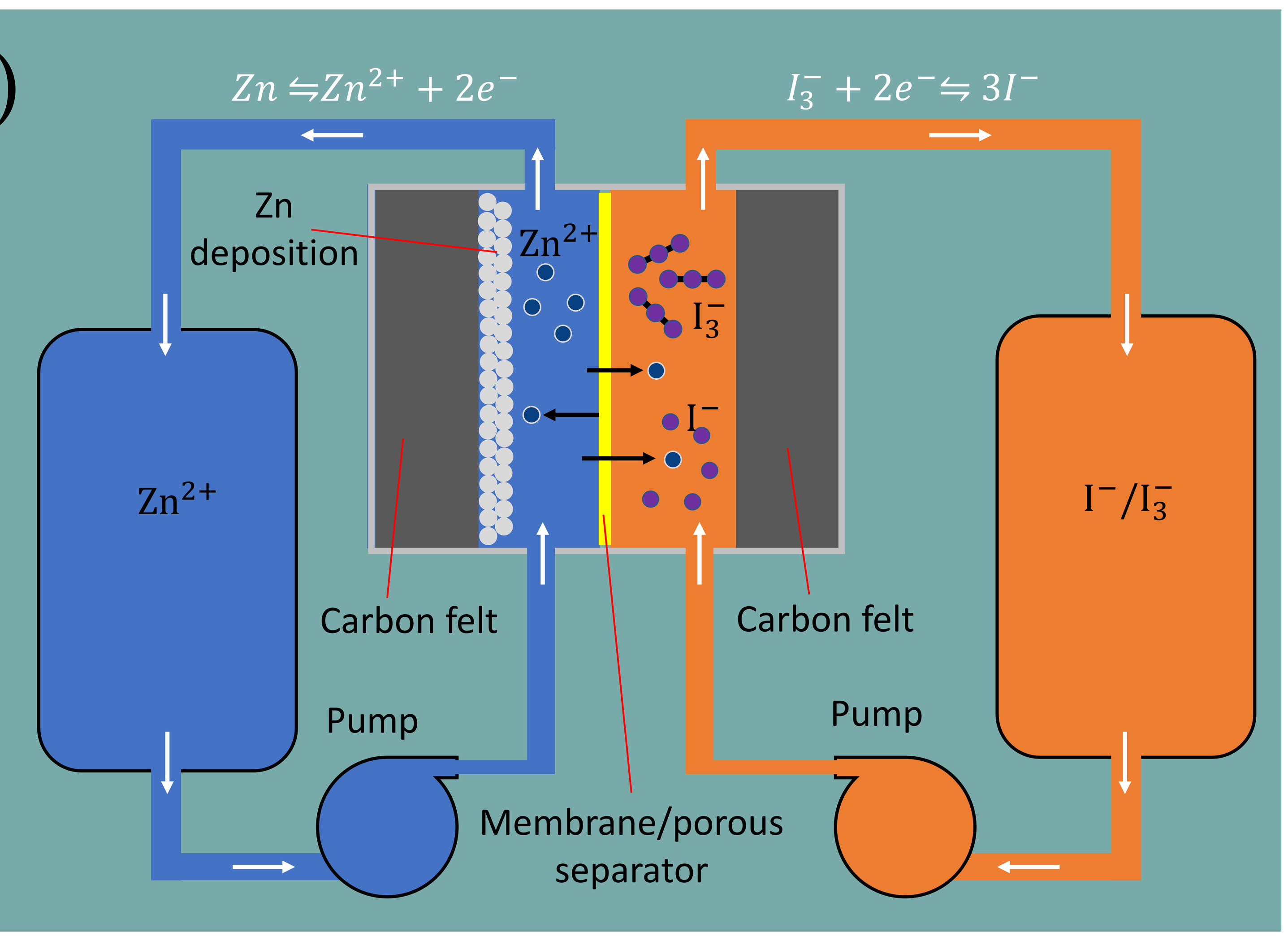
Zinc-iodine hybrid flow batteries (ZIHFBs)



Advantages

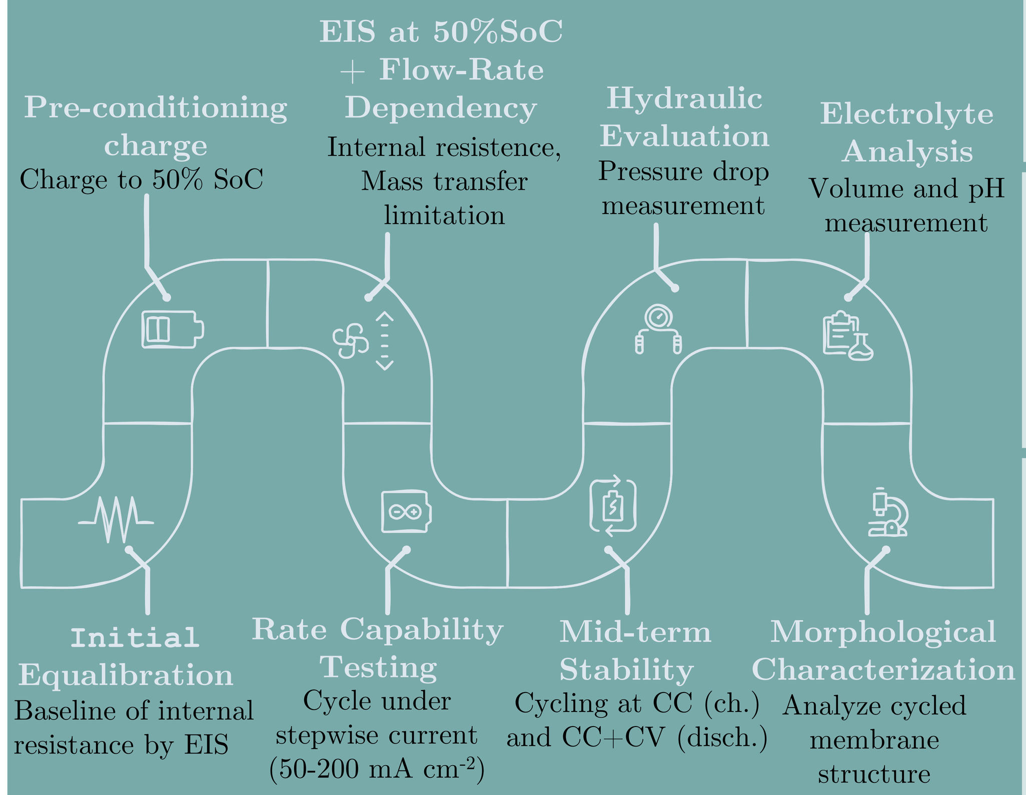
- ✓ High theoretical energy density (240 Wh l⁻¹)
- ✓ Abundant & Low-Cost Materials
- ✓ Non-flammable aqueous electrolytes
- ✓ pH near neutral
- ✓ Missible electrolytes

Challenges

- × Zinc dendritic growth → capacity losses
- × Active species crossover → self-discharge by I_3^-
- × Solid Iodine precipitation
- × Parasitic reactions → HER, passivation
- × Electrolyte volume imbalances

Methodology

Complex characterization of the single-cell



Standard conditions

Cycling experiments:

- 3D graphite felt
- 100 mA cm⁻²
- 80.4 mAh cm⁻²
- 60 ml | 60 ml
- 53.6 Ah l⁻¹
- 40°C
- 1M ZnI_2, 4M KI, 1.5M KCl

Permeation tests:

- 3D graphite felt
- Permeate: 0.45M KI + 0.35M KCl
- Retentate: Negolyte (50% SoC of SE)
- 60 ml | 60 ml

Cell and materials

- Hardware: Lab-scale flow cell (Pinflow, 20 cm² active area)
- Electrodes: Thermally activated rayon-based 3D carbon felts.
- Membranes: Commercial PFSA library with varying thickness (TH) and ion-exchange capacity (IEC). Activated 1h in DEMI water at 60°C.

Ex-situ permeation of active species:

- Zn^{2+} determination → chelatometric titration
  Zn^{2+}+EBT → ZnEBT (wine red)
  ZnEBT+$EDTA^{4-}$ → $Zn(EDTA)^{2-}$+EBT (blue)
- I_3^- permeation → UV-VIS spectroscopy – 288 and 351 nm
- I^- permeation → Ion-selective electrode – chloride interference – NOT DONE YET

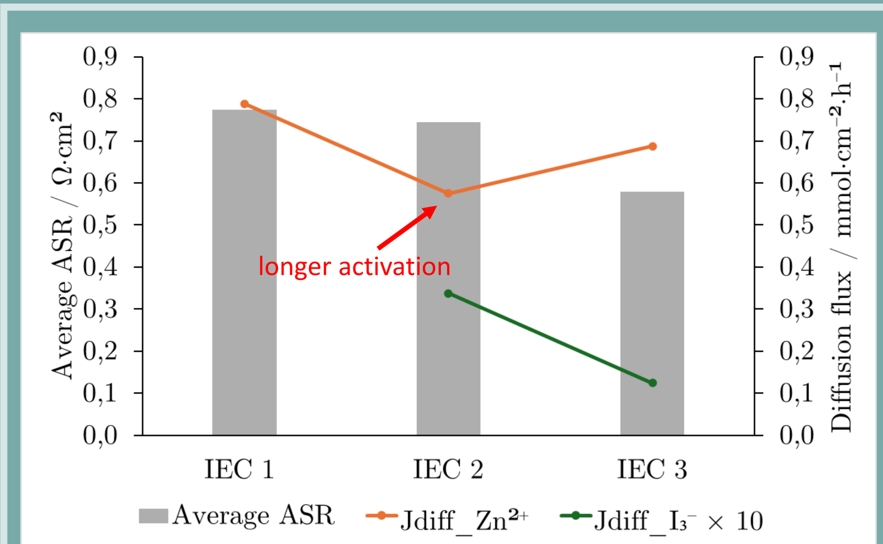
Aim of work

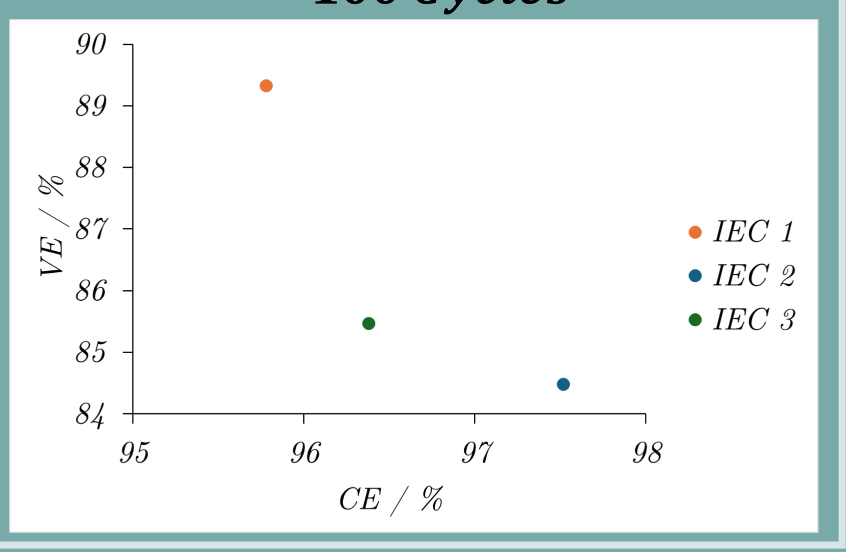
- **To evaluate** the medium-term cycling stability of ZIHFBs utilizing a series of commercial perfluorosulfonated membranes.
- **To compare** the direct impact of intrinsic membrane properties, specifically thickness and ion-exchange capacity (IEC), on Coulombic, voltage, and energy efficiencies.
- **To quantify** the crossover of active species by measuring the non-electrochemical permeation rates of Zn^{2+} and I_3^- ions under 50% SoC conditions.
- **To elucidate** the underlying mechanisms of irreversible cell degradation during high-Q_{areal} charging and evaluate restricted SoC windows as a preventative strategy *(Richtr et al., J. Mater. Chem. A)*.
- **To reveal** the optimal engineering trade-off between ionic conductivity and permoselectivity necessary for successful industrial scale-up.

Results:

Effect of membrane IEC (IEC 1 < IEC 2 < IEC 3)

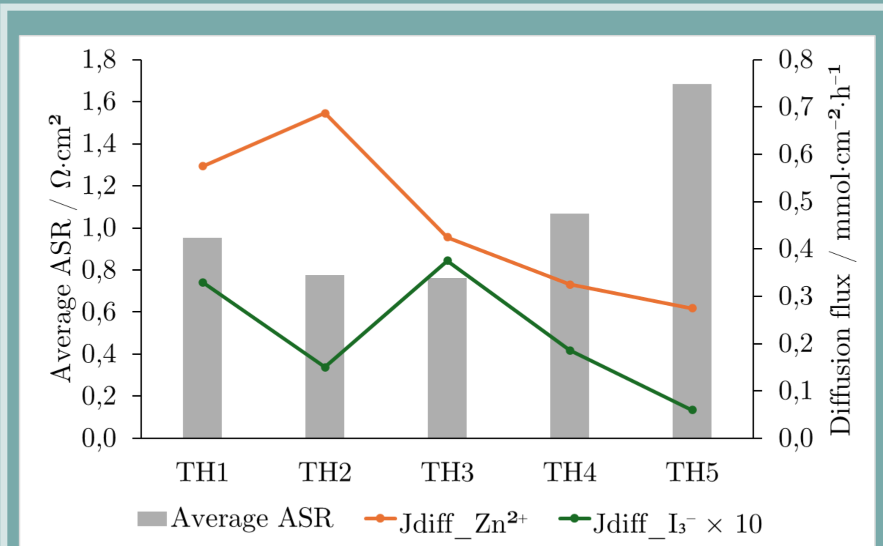
100 Cycles

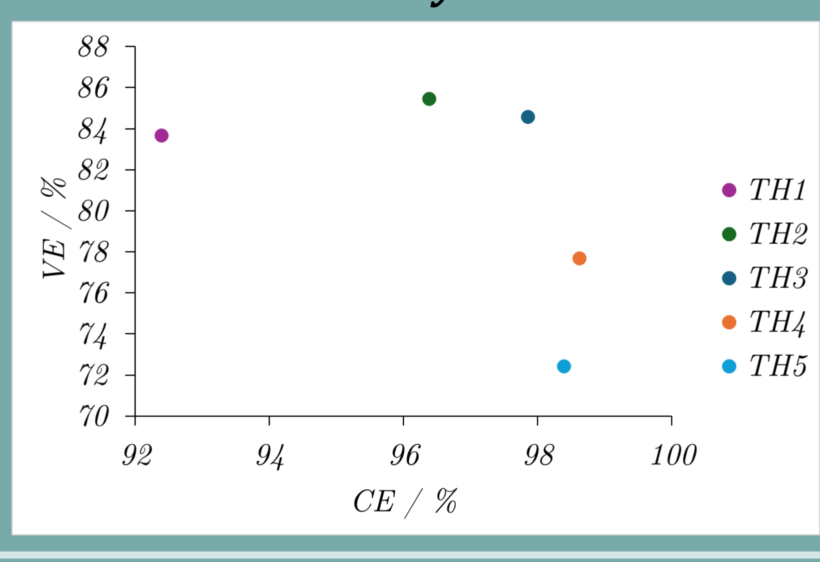




Effect of membrane thickness (TH1 <…<TH5)

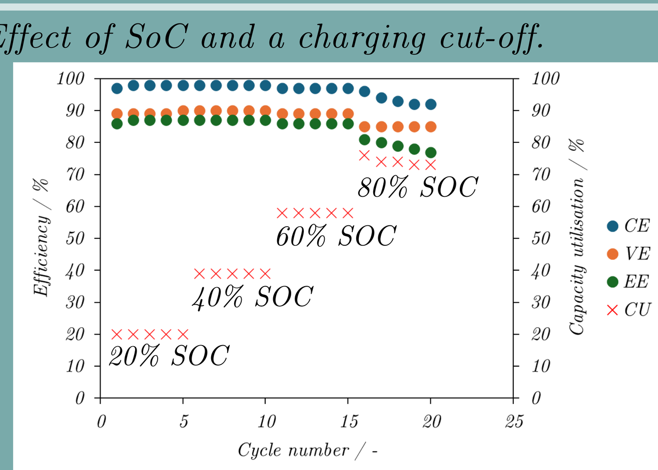
100 Cycles

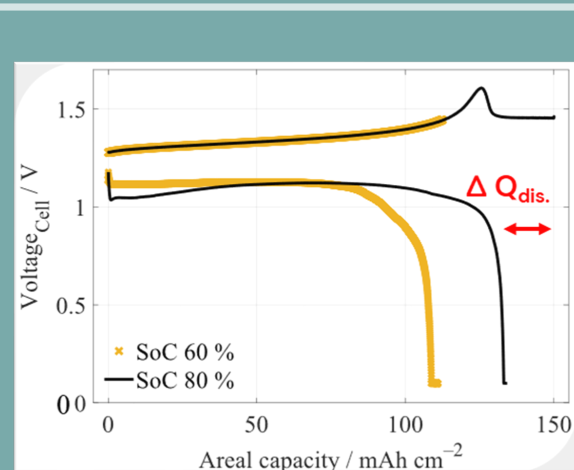




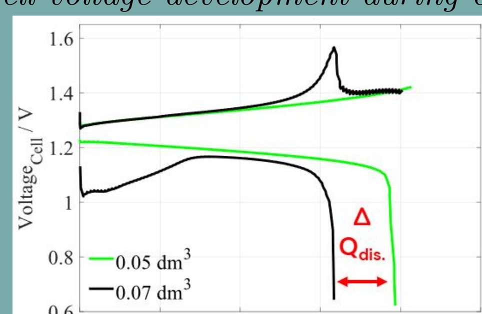
Operational restriction

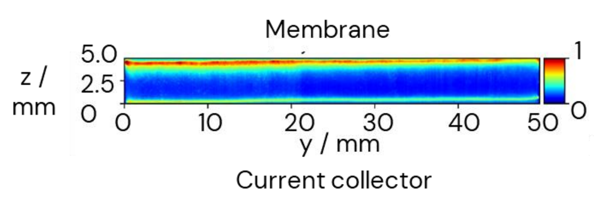
Effect of SoC and a charging cut-off.

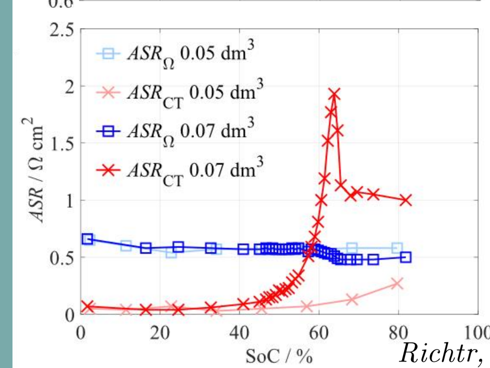


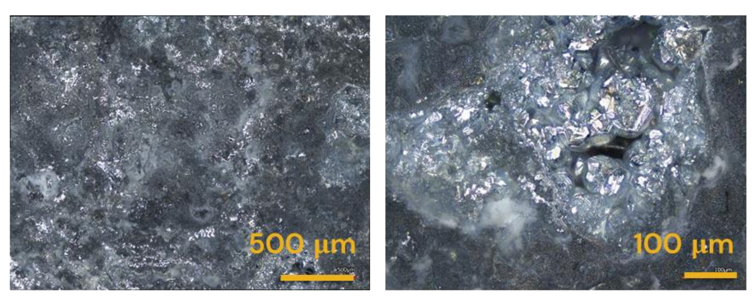


Cell voltage development during cycling at 100 mA cm⁻² for different negolyte volumes



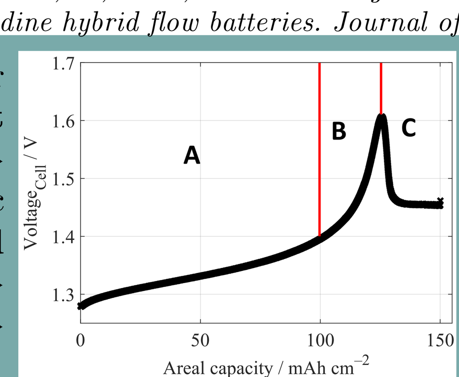


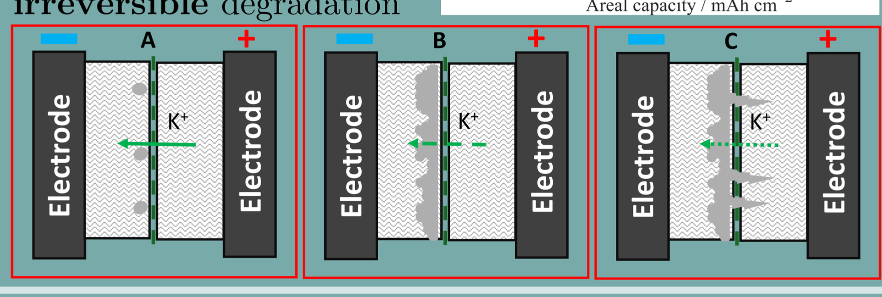




Richtr, P., et al., Understanding the degradation process in zinc–iodine hybrid flow batteries. Journal of Materials Chemistry A, 2026.

Zn accumulates near **membrane** → **compact** layer (porosity 0.93 → 0.15) → **limited** ionic transport → promoted **dendrite** formation → **membrane** piercing → **irreversible** degradation



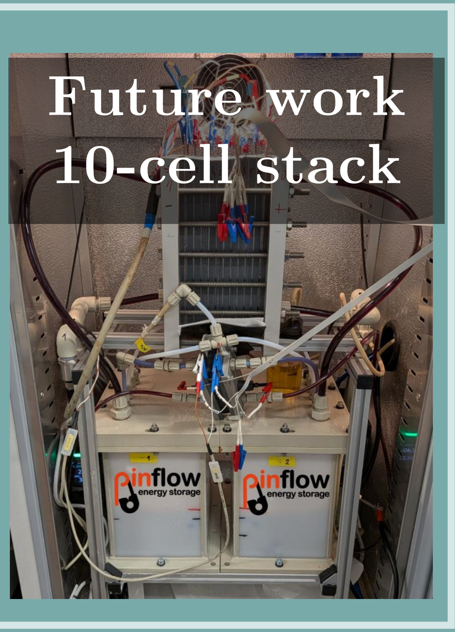


So called **"voltaic bulge"** is an anomalous distortion on the voltage-time **curve representing a sudden spike in charge-transfer** resistance ASR_{CT} rather than a simple ohmic loss. It physically represents the exact moment the electrode becomes 'choked' by a compact zinc layer, drastically limiting reactant accessibility.

Conclusion

- **Membrane Thickness Trade-off:** Increasing the membrane thickness successfully minimizes active species crossover but simultaneously increases the intrinsic Area Specific Resistance (ASR). This forces a compromise between preventing self-discharge and maintaining high Voltage Efficiency (VE).
- **Role of Ion-Exchange Capacity (IEC):** Variations in IEC impact the crossover of active species. Careful optimization of the polymer matrix properties is essential to strike a balance between necessary ionic conductivity and perm-selectivity.
- **The "Voltaic Bulge" Phenomenon:** This anomalous voltage curve distortion serves as a critical warning of structural failure. It represents a sudden spike in charge-transfer resistance caused by a compact zinc layer that limits reactant accessibility and forces destructive dendritic growth toward the membrane.
- **Operational Mitigation Strategy:** Irreversible degradation and membrane piercing can be successfully prevented by applying strict operational constraints: Limiting the State of Charge (SoC) window and voltage cut-offs maintains membrane integrity and ensures medium-term cycling stability.

Future work
10-cell stack



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