Real-time half-cell diagnostics of capacity fade mechanisms in naphthalene diimide-based aqueous organic flow battery

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Introduction

Why NDI-based AORFB?

- Two-electron redox capability → high theoretical capacity [1, 2]
- Neutral pH operation, tunable molecular design

Problem with current diagnostics:

- Coulomb counting & full-cell OCV cannot resolve individual half-cell SOCs [3, 4, 5]
- mpossible to identify **which electrode** drives capacity fade

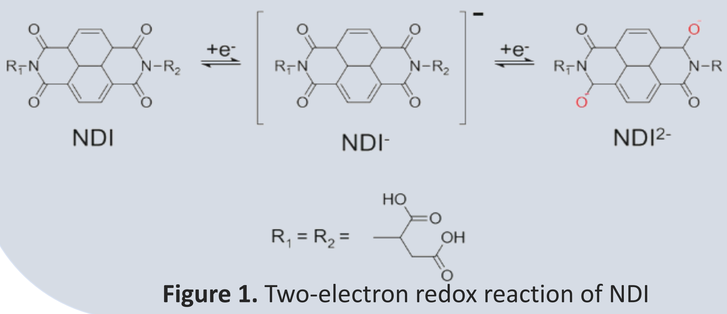

Figure 1. Two-electron redox reaction of NDI

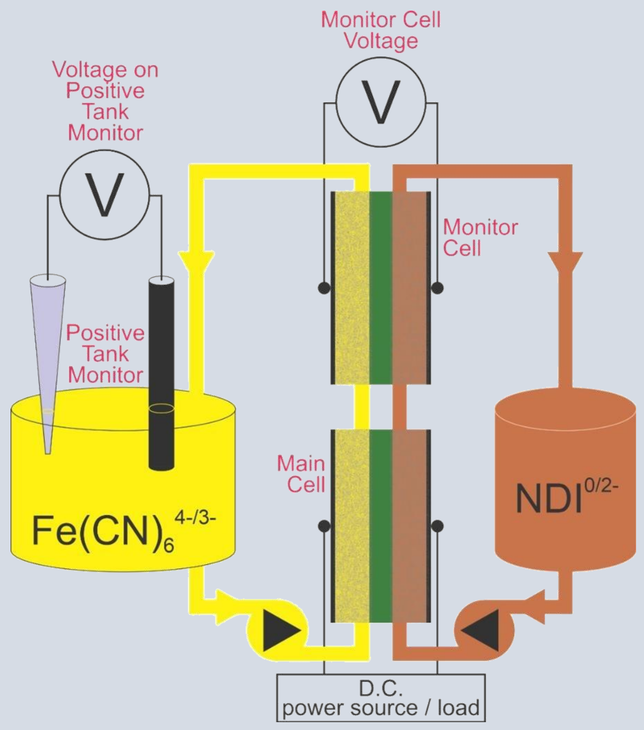

Figure 2. Schematic of the ADRFB with *in situ* zero-current potentiometry monitoring approach..

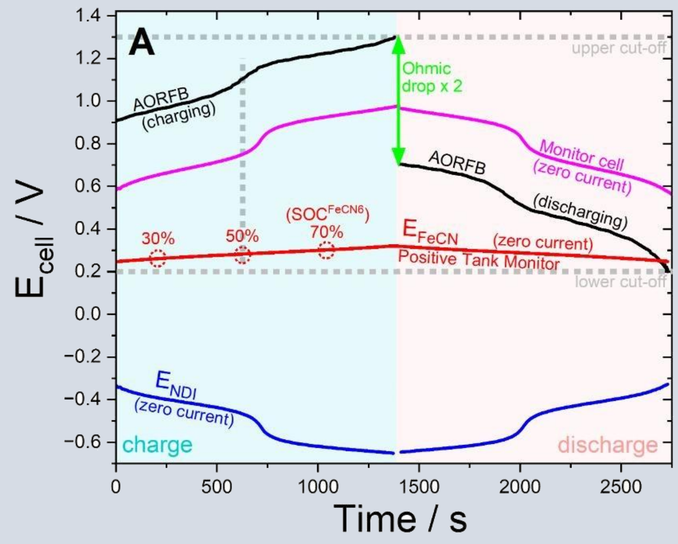

Figure 3 Cell voltage (E_{cell}) vs. time during galvanostatic cycling.

This work:

•In situ zero-current potentiometry → independent real-time monitoring of FeCN and NDI electrode potentials

•Nernst-based analytical SOC mapping for each half-cell [6]

Result

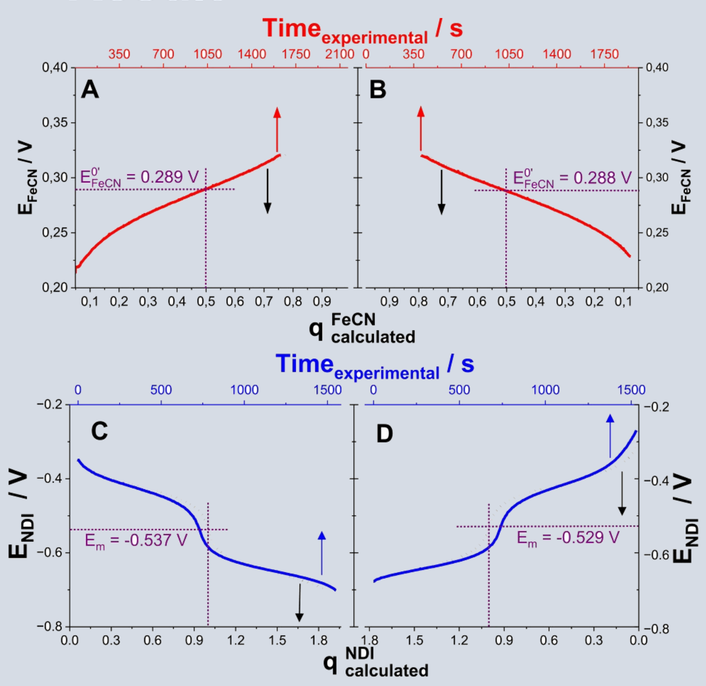

Figure 4. Experimental half-cell potentials of FeCN and NDI follow Nernst-predicted SOC profiles.

Nernstian SOC Tracking

•Experimental half-cell potentials of both FeCN and NDI electrodes closely follow Nernst-predicted SOC profiles

•Confirms **ideal thermodynamic behavior** despite non-ideal concentrated electrolyte conditions

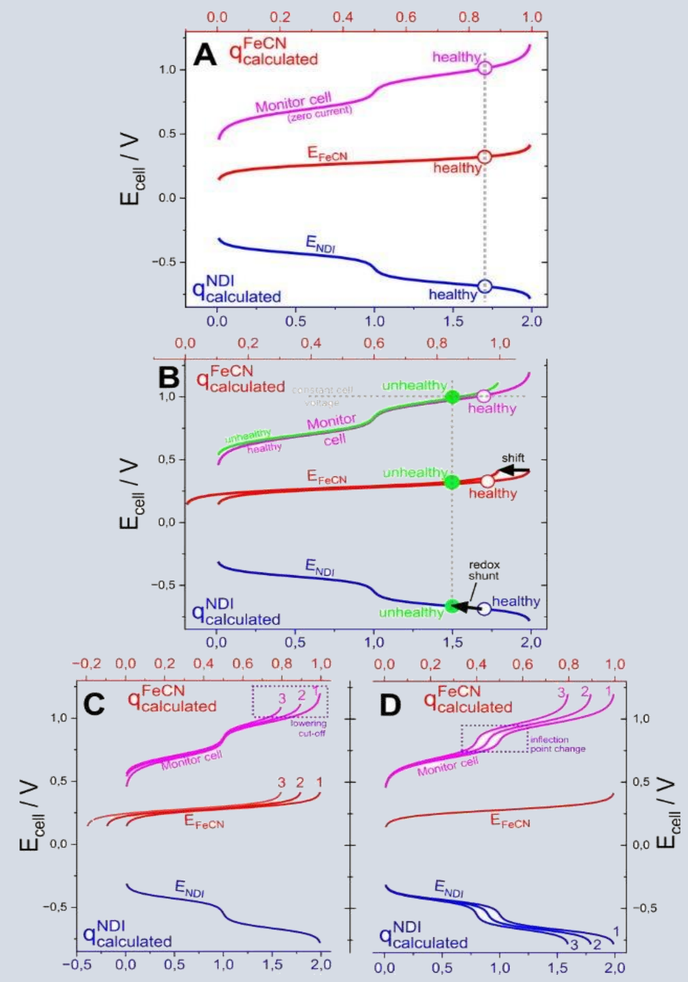

Figure 5. (A) Healthy well-balanced AORFB; (B) appearance of the charge disbalance due to the redox shunt on negative electrode resulted in positive electrode limitationTwo degradation signatures: **(C)** redox shunt — reversible charge imbalance; **(D)** NDI hydrolysis — irreversible active material loss

Two Distinct Degradation Signatures

•**Redox shunt** (O_2 ingress):

- Excess charge accumulates on NDI side → charge imbalance
- Cut-off voltage **decreases**, inflection point **unchanged**
- Reversible — capacity restored by positive electrolyte rebalancing

•**Irreversible degradation** (NDI hydrolysis):

- Active NDI removed from redox equilibrium
- SOC profile **compresses**, inflection point **shifts**
- Confirmed by HPLC-MS: NDI monoimide detected post-mortem

Conclusion

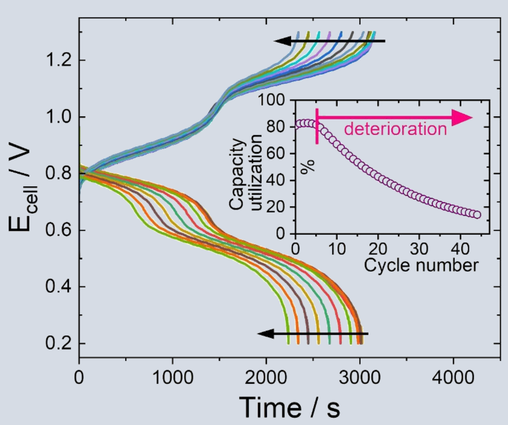

Figure 6. Capacity fade over extended cycling due to co-existing degradation mechanisms.

•**In situ zero-current potentiometry** enables independent, real-time SOC monitoring of both FeCN and NDI half-cells

•Nernst-based analytical framework validated experimentally for both electrodes

•Two **co-existing degradation mechanisms** identified and decoupled:

- •**Redox shunt** — reversible, O_2-driven charge imbalance
- • **Irreversible degradation** — NDI hydrolysis, active material loss

•Diagnostic framework guides **targeted mitigation strategies**:

- Improved sealing → suppress O_2 ingress
- NDI molecular stabilization → suppress hydrolysis

•Method is **general** — applicable to other multi-electron organic RFB chemistries

References

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Read the full paper:

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