Rechargeable oxygen ion batteries based on mixed conducting oxides

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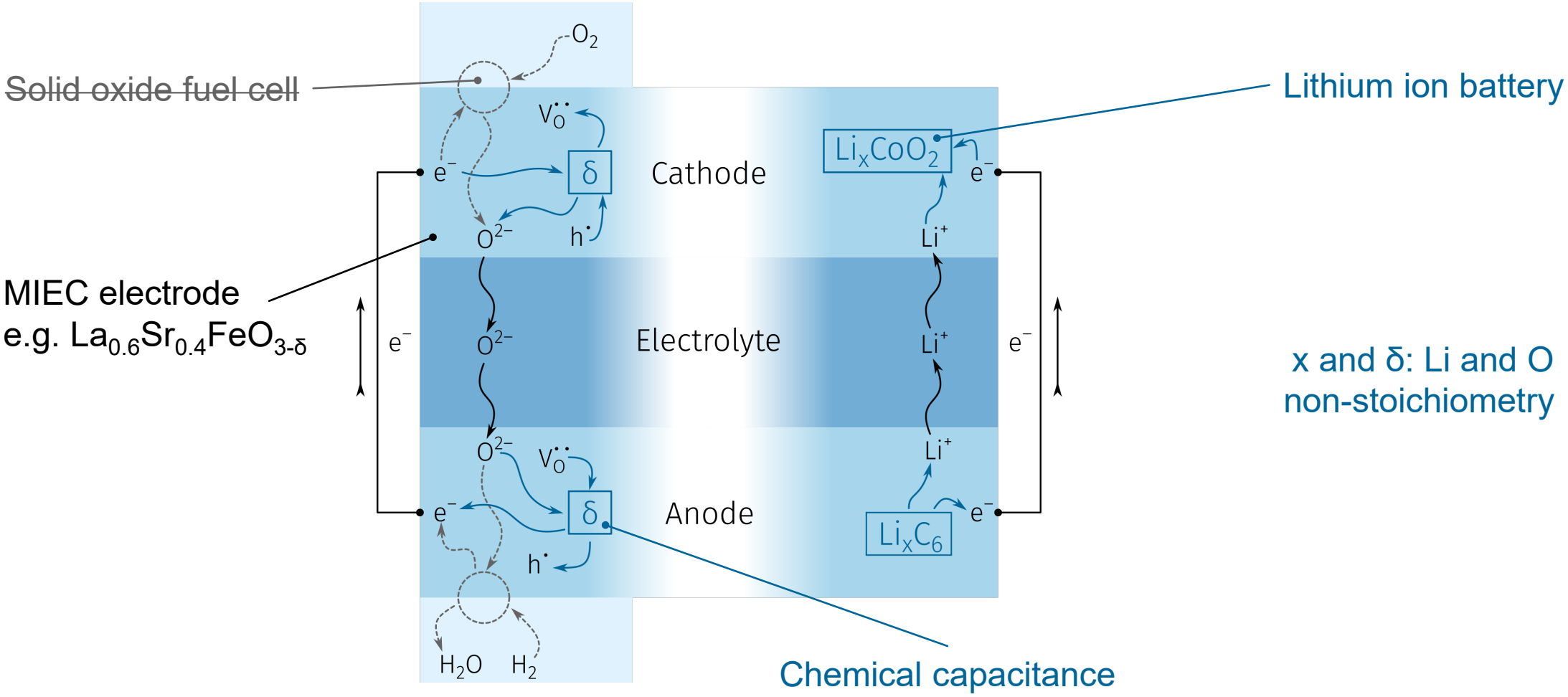
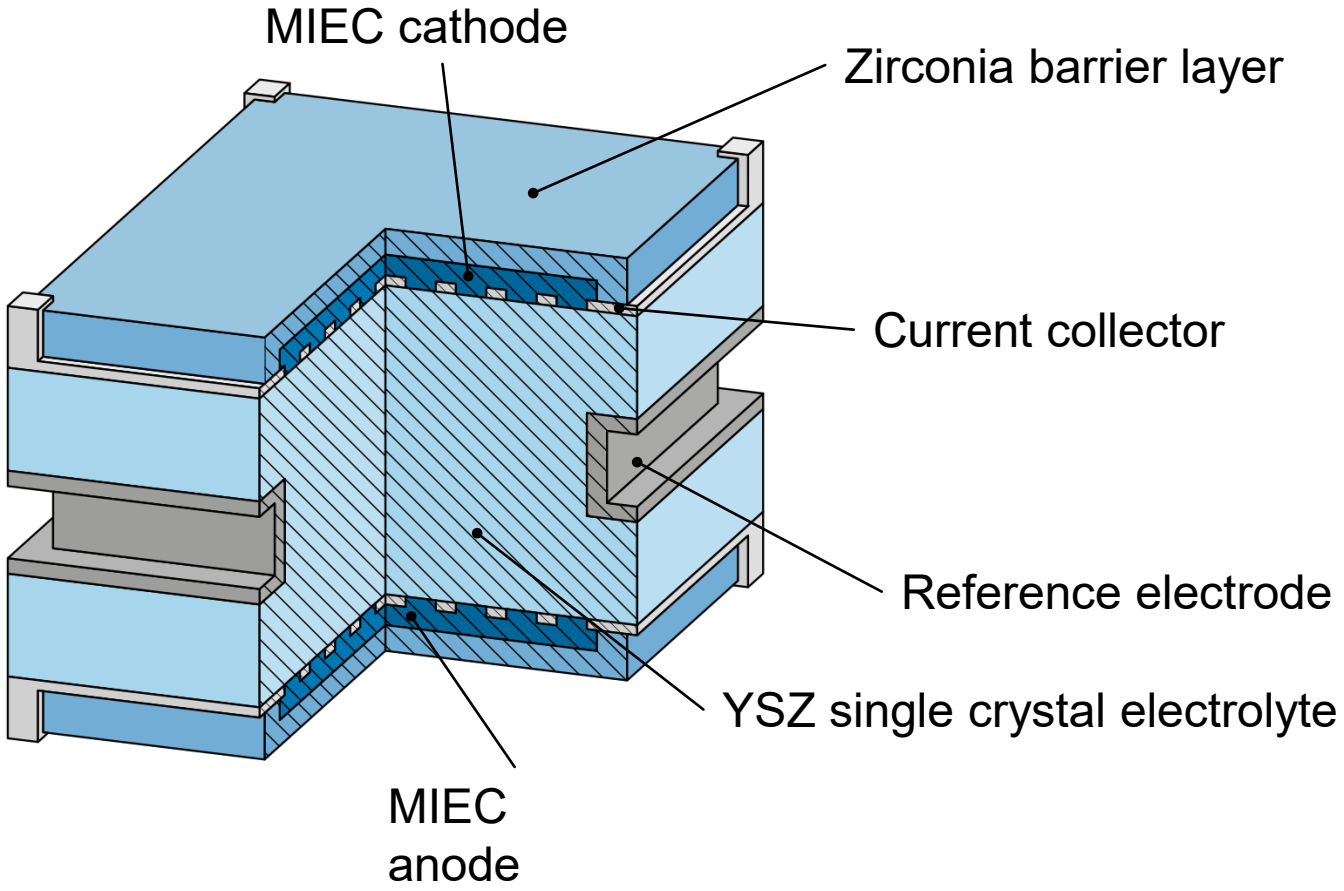
Operation principle



Experimental approach

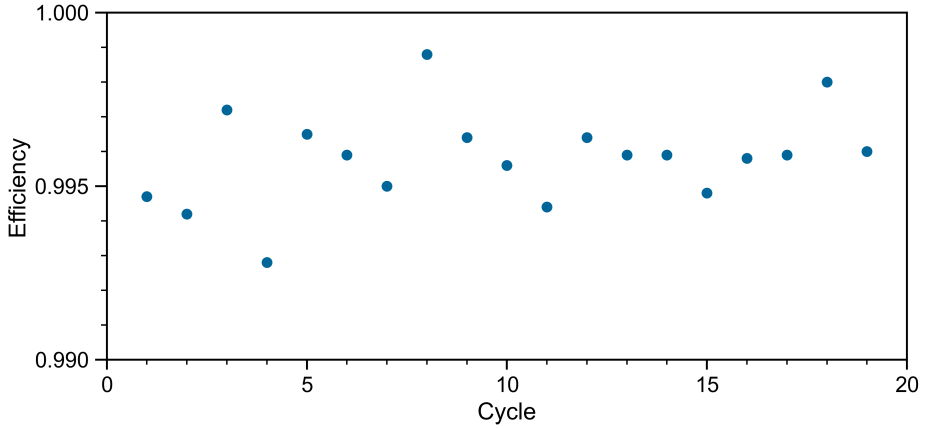
- Thin film model systems
- Pulsed laser deposition
- Three electrode setup

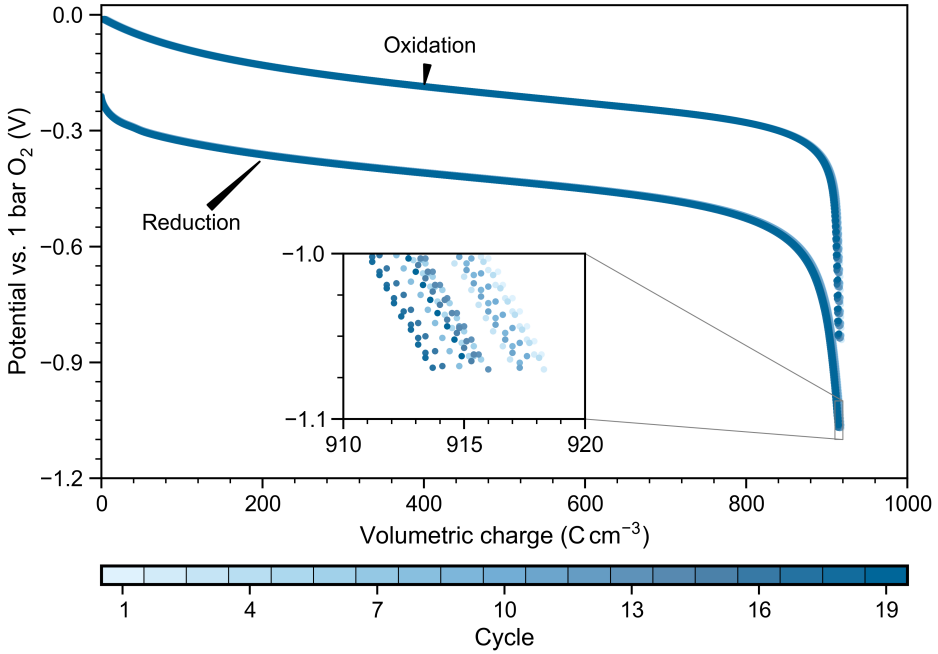
- Electrochemical impedance spectroscopy
- DC charge/voltage measurements



$La_{0.6}Sr_{0.4}FeO_{3-\delta}$ electrodes - Charge voltage characteristics

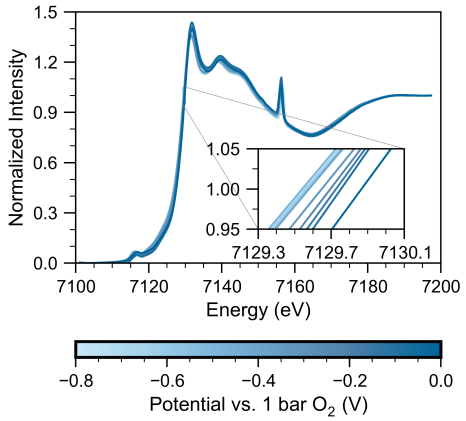
- 915 C cm^{-3} at -0.3 V vs. 1 bar O_2 (255 mA h cm^{-3})
- <0.1 % capacity loss per cycle
- >99 % coulomb efficiency

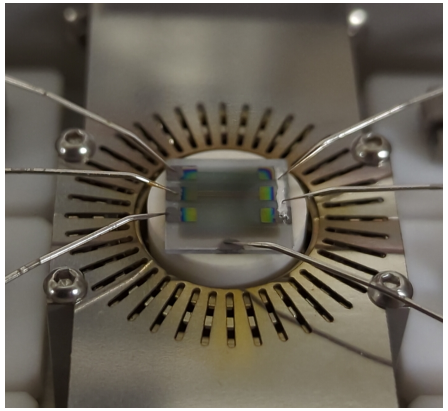


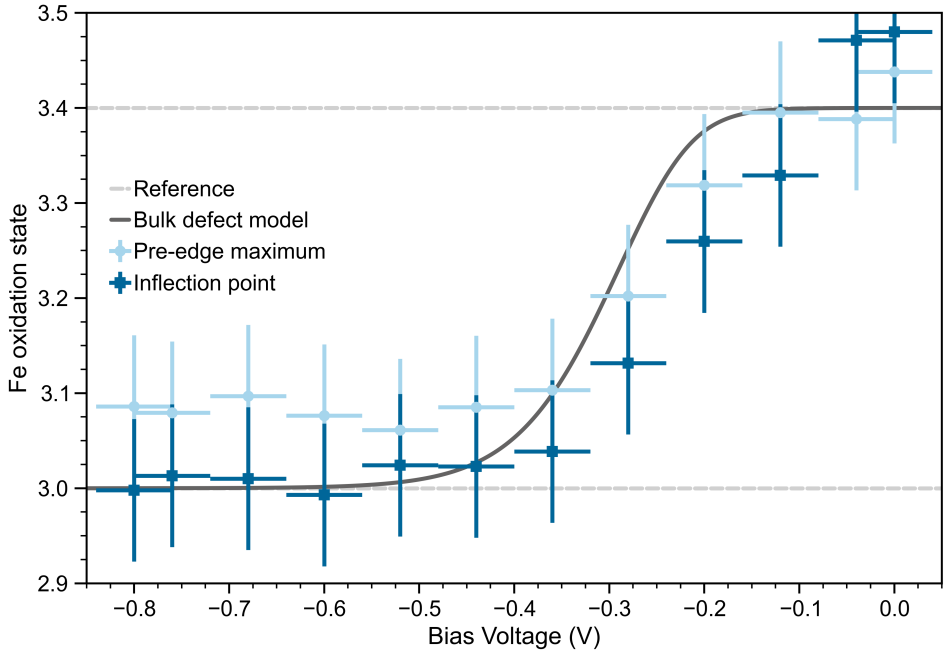


450 nm LSF film, 350 °C, 58 µA cm^{-2} (5 C), 25 Pa O_2

In-situ synchrotron X-ray absorption spectroscopy



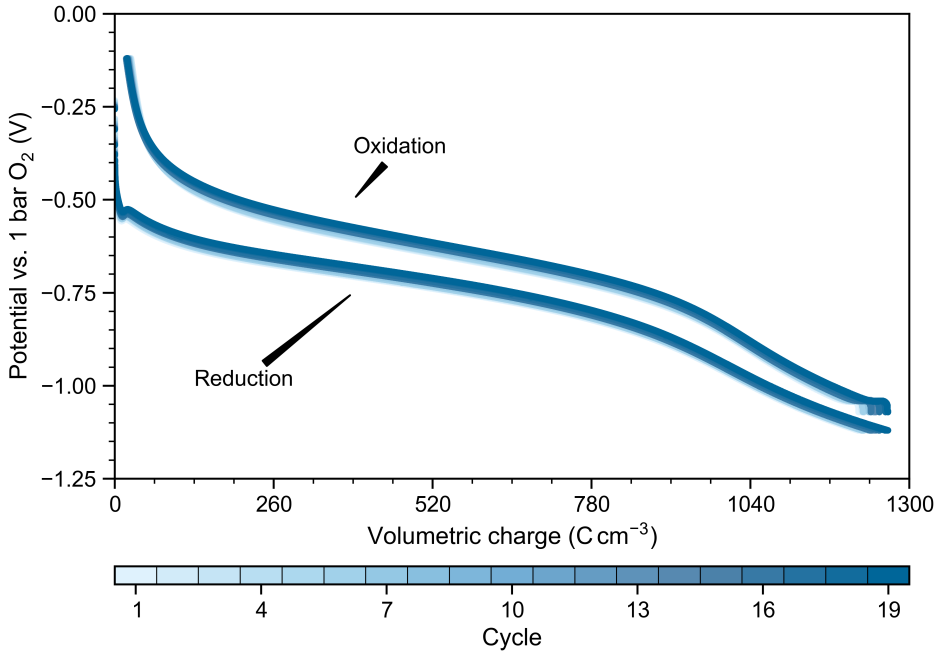




200 nm LSF film, 350 °C, 100 kPa O_2

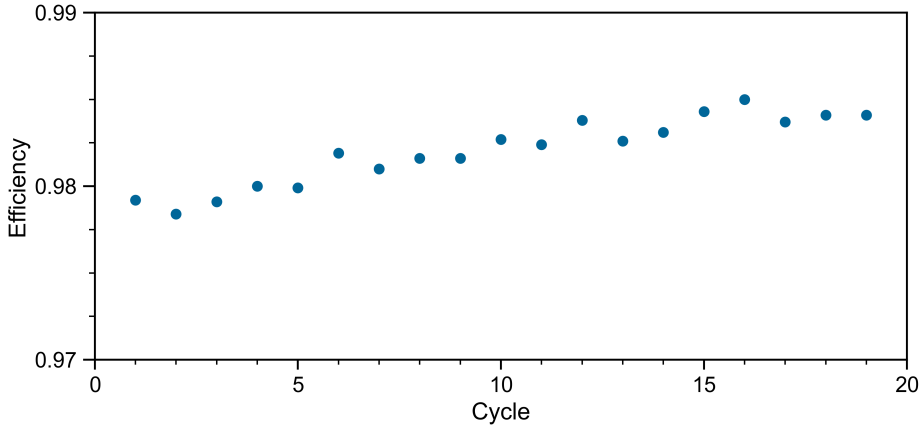
- Electrode charge/discharge leads to Fe oxidation state change
- $2\,\mathrm{Fe}_{\mathrm{Fe}}^{\mathrm{x}} + \mathrm{V}_{\mathrm{O}}^{\cdot\cdot} + \mathrm{O}^{2-} \rightleftharpoons 2\,\mathrm{Fe}_{\mathrm{Fe}}^{\cdot} + \mathrm{O}_{\mathrm{O}}^{\mathrm{x}} + 2\mathrm{e}^{-}$
- Agrees with bulk defect model

$La_{0.5}Sr_{0.5}Cr_{0.2}Mn_{0.8}O_{3-\delta}$ anodes



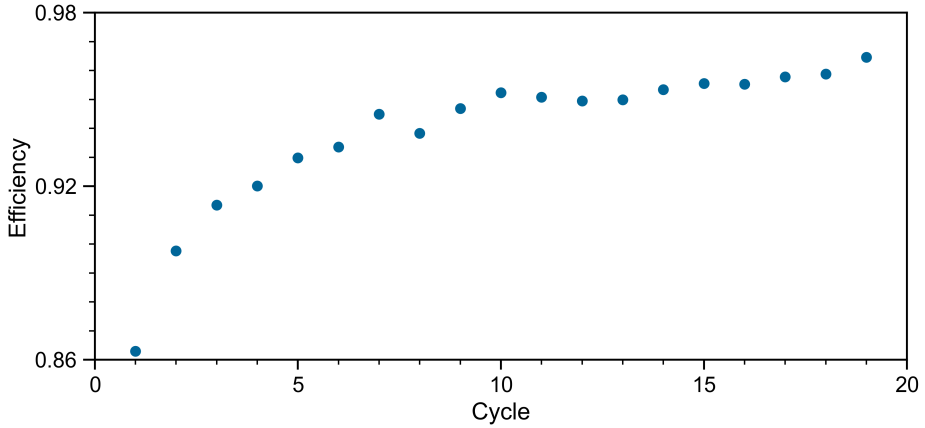
630 nm LSCrMn film, 400 °C, 17 µA cm^{-2} (0.8 C), 25 Pa O_2

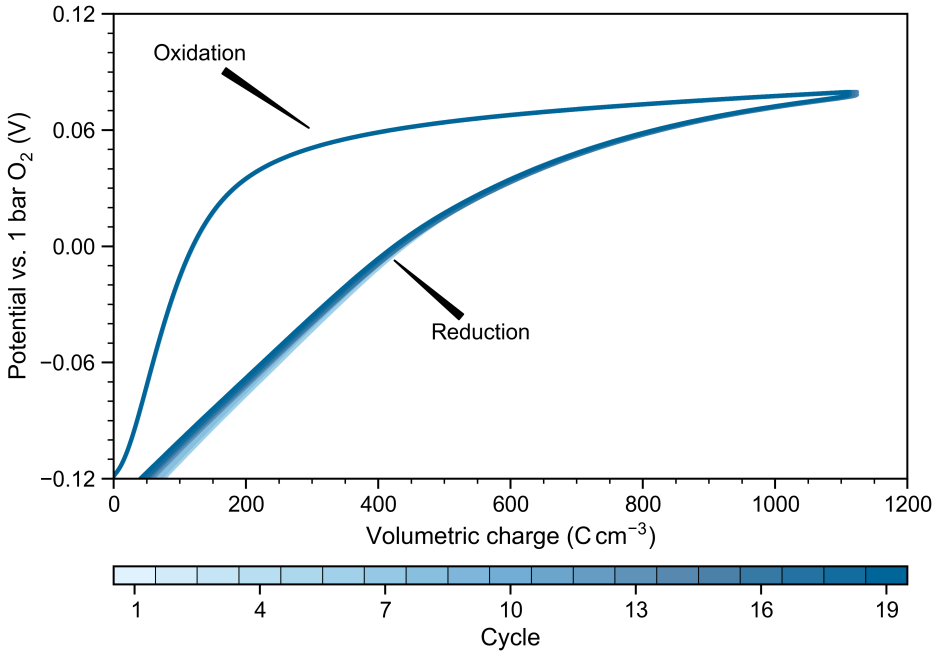
- 1250 C cm^{-3} at -0.6 V vs. 1 bar O_2 (350 mA h cm^{-3})
- Up to 3500 C cm^{-3} at -2 V
- Poster by B. Wagner



$La_2NiO_{4+\delta}$ cathodes

- Intercalation of oxygen as interstitials
- High half cell potential
- $2\,Ni_{Ni}^{x} + O^{2-} \rightleftharpoons 2\,Ni_{Ni}^{\cdot} + O_i'' + 2e^-$

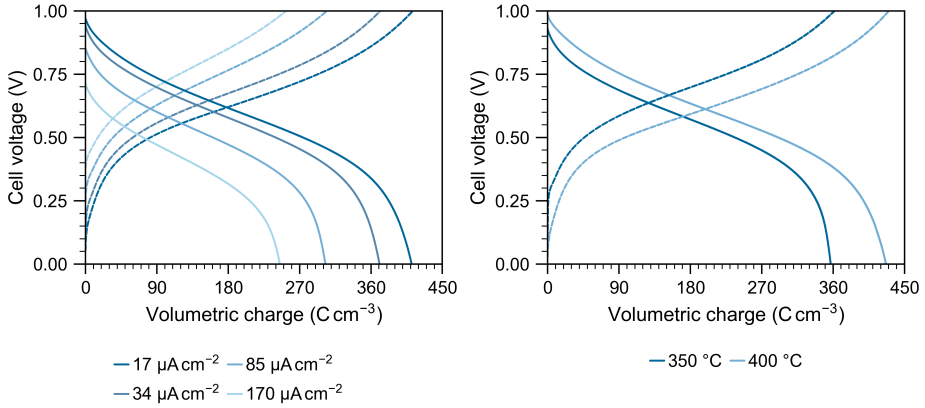




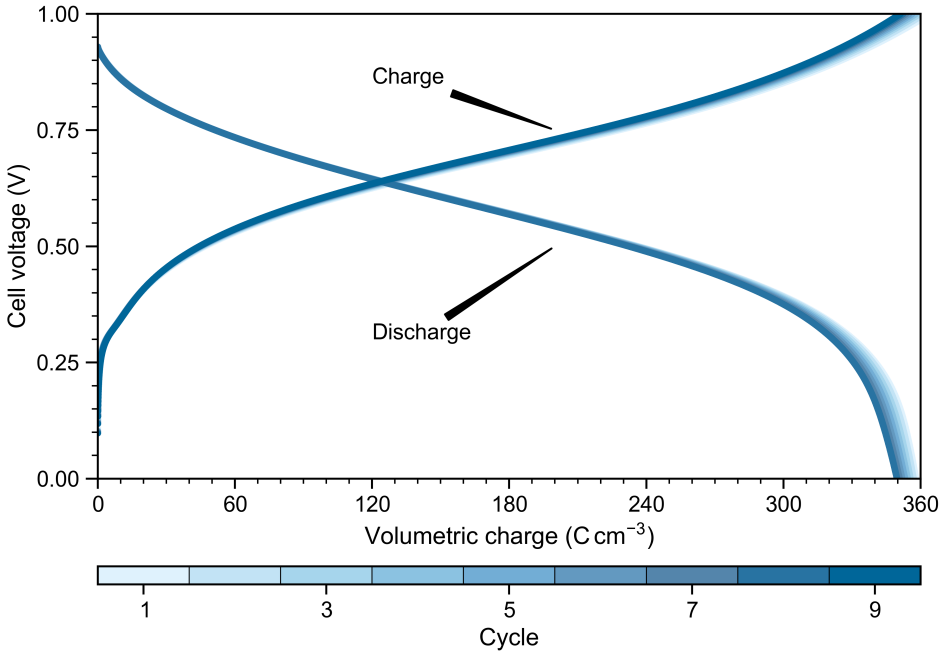
200 nm LNO film, 400 °C, 17 µA cm^{-2} , 1000 Pa O_2, prepared by LMGP, Grenoble

Complete oxygen ion battery: LSCrMn I YSZ-SC I LSF

- 420 C cm^{-3} at 0.6 V
- 250 J cm^{-3}
- >99 % coulomb efficiency



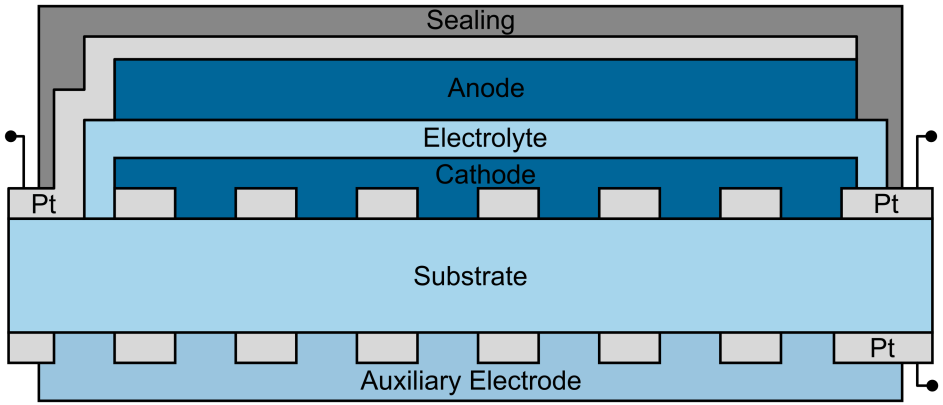
320 nm LSF, 192 nm LSCrMn, 25 Pa O_2

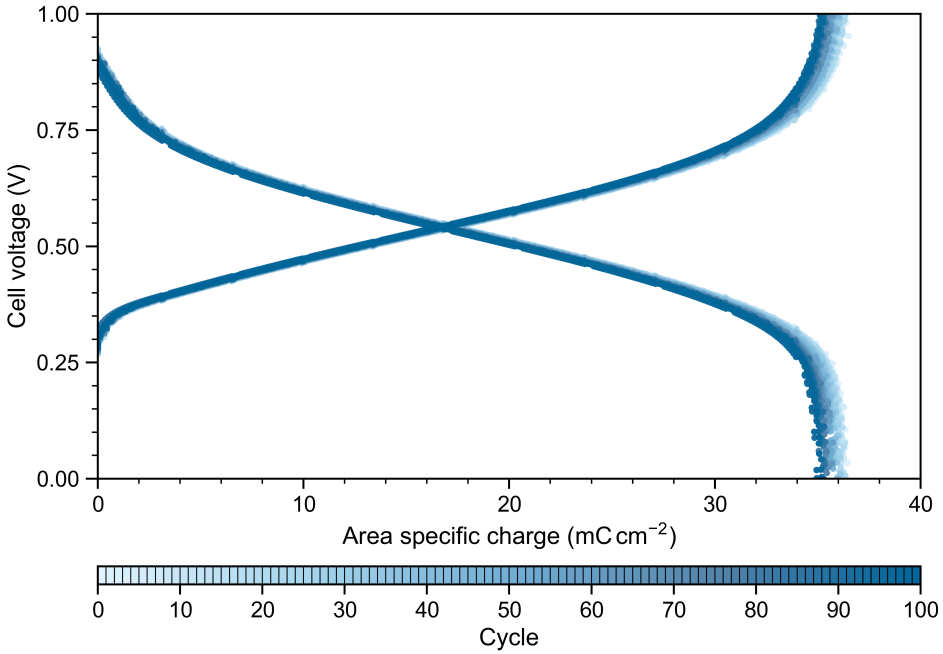


320 nm LSF, 192 nm LSCrMn, 350 °C, 8.5 µA cm^{-2} (1.6 C), 25 Pa O_2

Full cell battery with thin film electrolyte

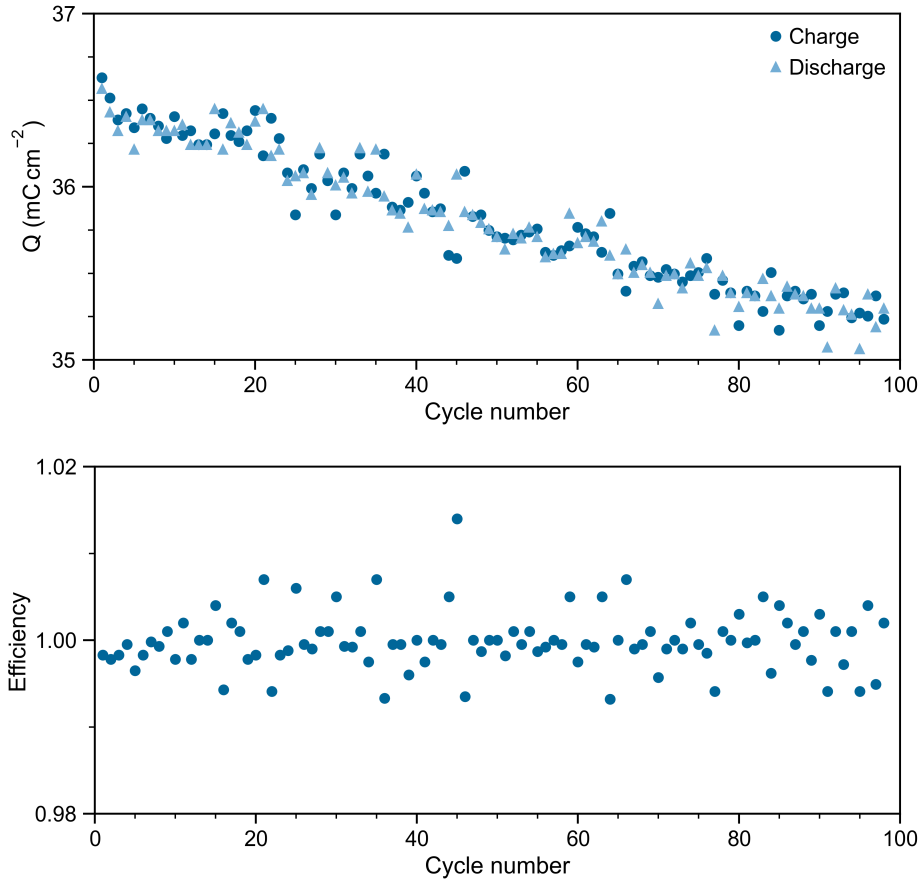
- Thin film electrolyte – 800 nm
- Reactive DC sputtering from Y/Zr metal target





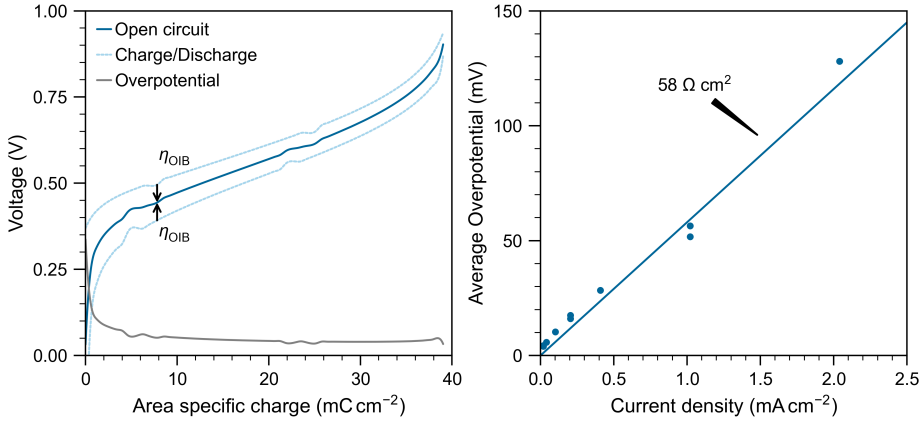
500 nm LSF, 400 nm LSCrMn, 350 °C, 200 µA cm^{-2} (20 C), 1 kPa O_2

Full cell battery with thin film electrolyte



500 nm LSF, 400 nm LSCrMn, 350 °C, 200 µA cm^{-2} (20 C), 1 kPa O_2

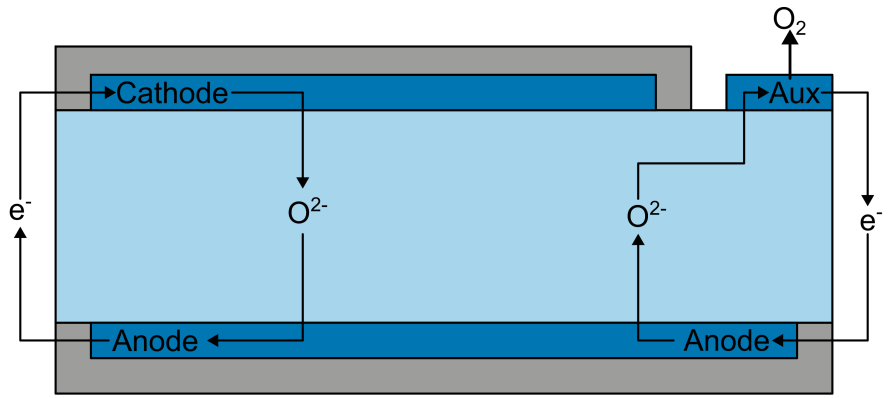
- Interface resistance relevant
- < 0.05 % charge lost per cycle
- Cell stable over >2000 cycles in total (with regeneration steps)

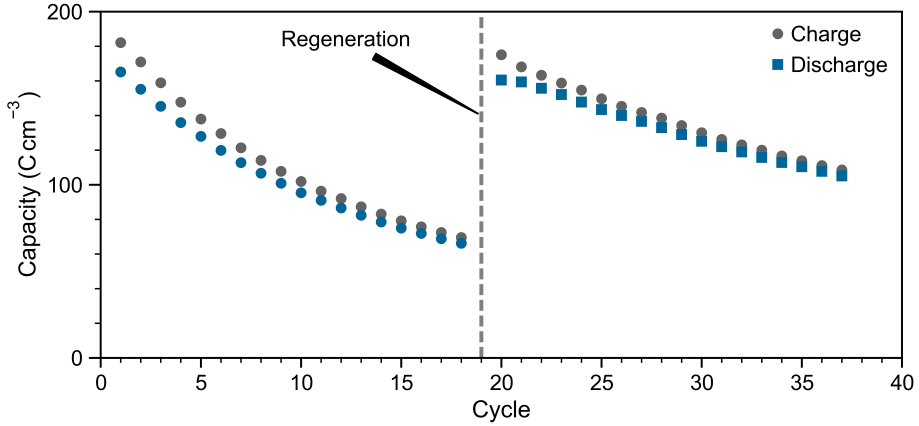


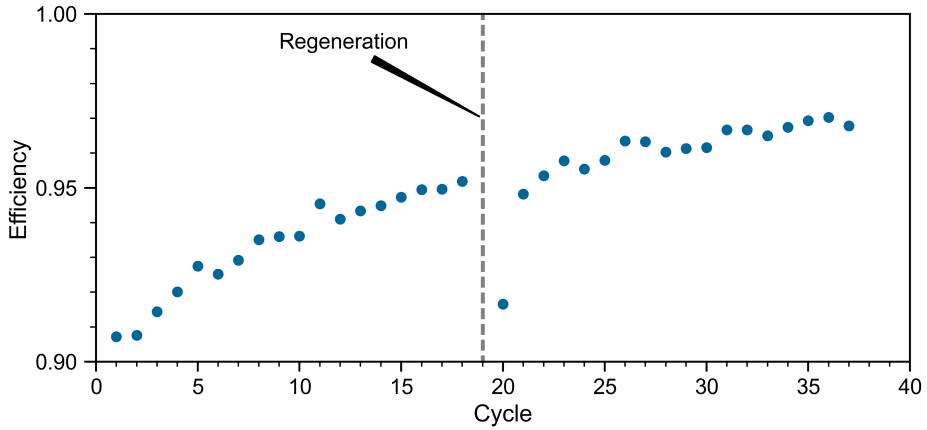
500 nm LSF, 400 nm LSCrMn, 350 °C, 1000 µA cm^{-2}, 1 kPa O_2

Regeneration of degraded cell capacity

- Removal of leaked oxygen via auxiliary electrode
- Cell capacity repeatedly regenerable



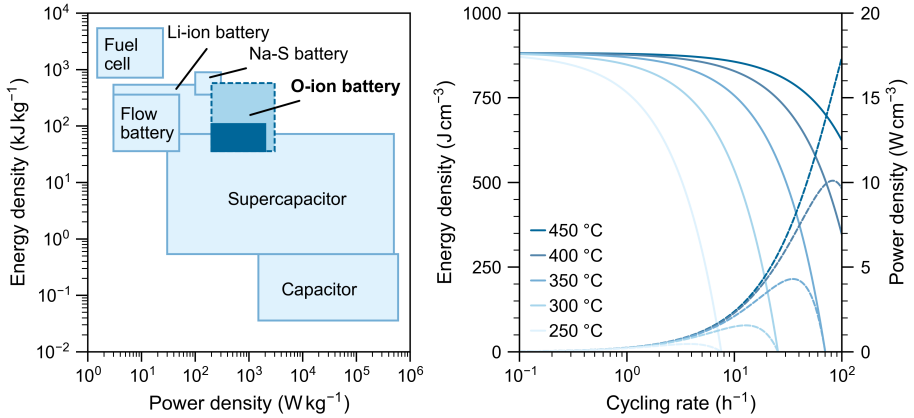




320 nm LSF, 192 nm LSCrMn, 350 °C, 17 µA cm^{-2} (3.2 C), 1 kPa O_2

The potential of oxygen ion batteries

- Cell voltage: 1V
- Electrode capacity: 2250 C cm^{-3}
- 1 µm electrolyte
- 25 µm electrodes



- Energy: 900 J cm^{-3}
- Charge rate: 1 - 100 h^{-1}
- Power: 1 - 18 W cm^{-3}

- Abundant elements (Fe, Cr, Mn, Ti, Ca, Sr, …)
- Non-flammable, non-toxic oxides
- Regenerable cell capacity

Conclusions

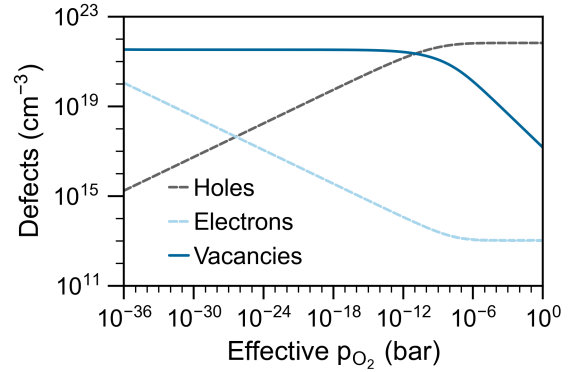
- High temperature energy storage via variable oxygen stoichiometry
- Non-flammable, non-toxic oxides, not reliant on critical raw elements
- Cell capacity repeatedly regenerable via atmosphere exchange

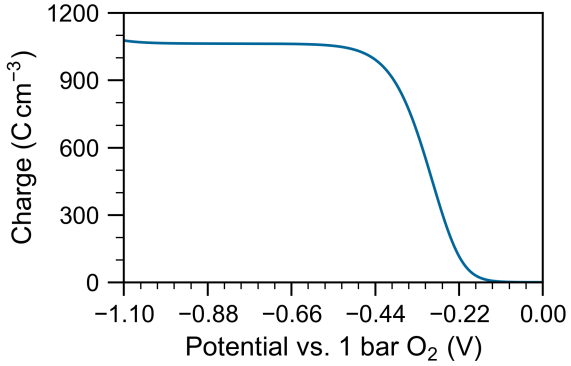
Thank you for your attention!

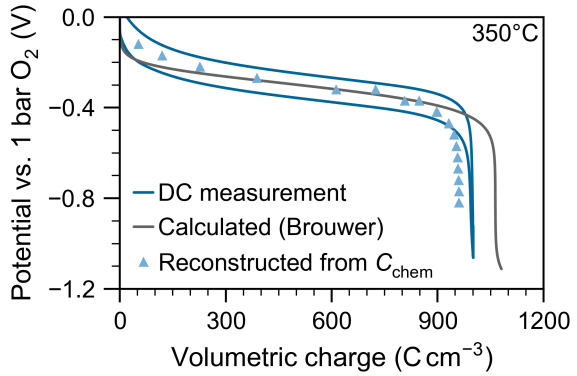
For more information, please visit :

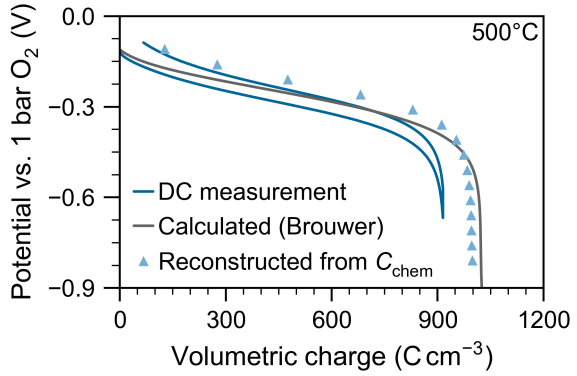
- Schmid, M. Krammer, and J. Fleig, “Rechargeable Oxide Ion Batteries Based on Mixed Conducting Oxide Electrodes,” *Advanced Energy Materials*, **2023**, *13*, 2203789.

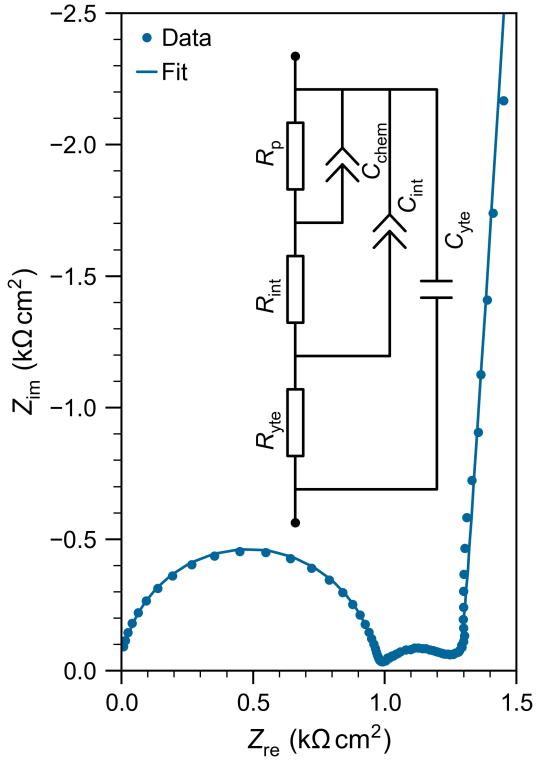
LSF electrodes – A defect chemical explanation







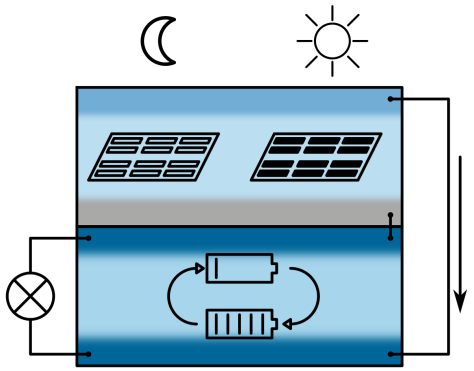


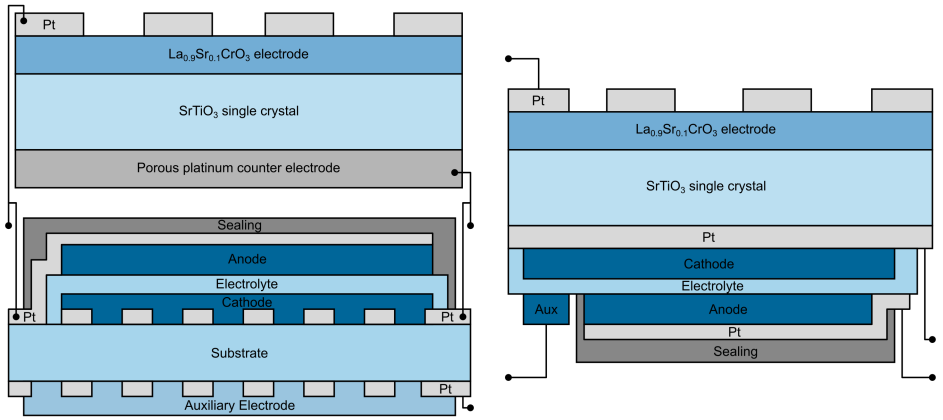


$$\Delta Q = 2F[V_O^{\cdot\cdot}] \quad U = \frac{RT}{4F}\ln\left(\frac{p_{O_2}}{1\ \text{bar}}\right)$$

$$Q(U) = \int C_{chem}\, dU \quad C_{chem} = \frac{F^2}{RT}\left(\frac{1}{4[V_O^{\cdot\cdot}]} + \frac{1}{[h^{\cdot}]}\right)^{-1}$$

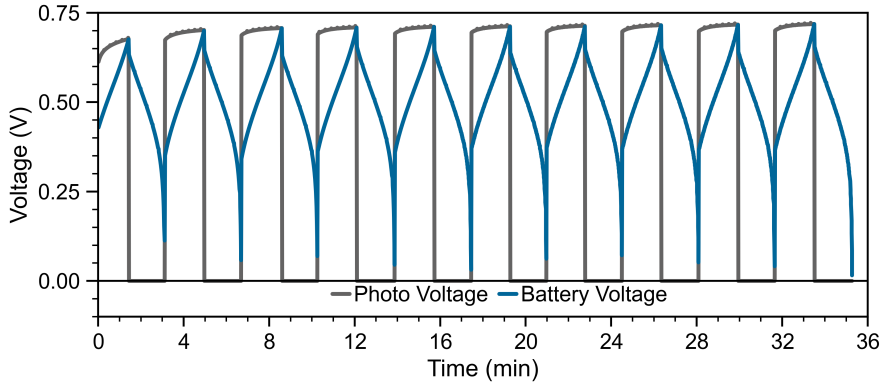
The Harvestore concept





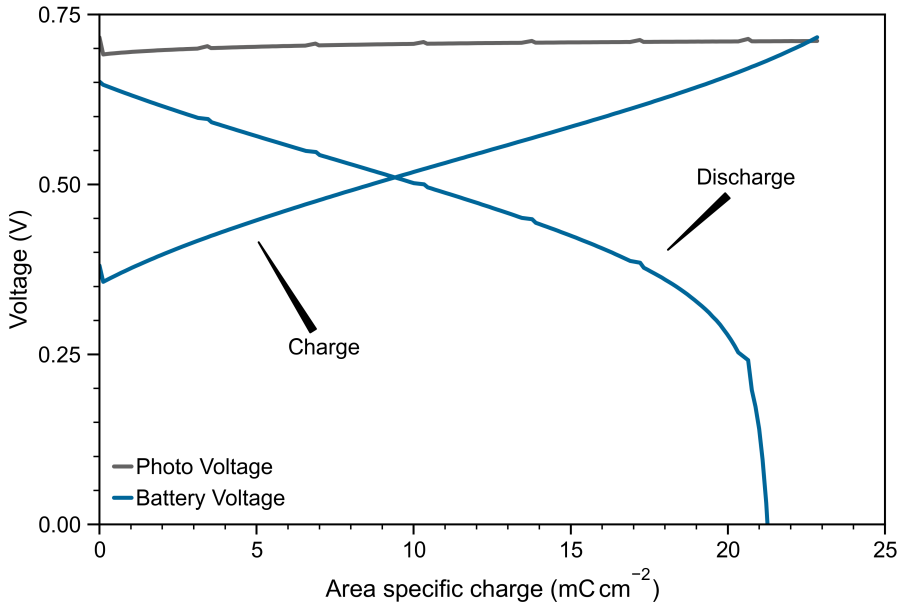
- Thin film oxygen ion battery coupled to $SrTiO_3$ PV cell
- Battery charged by photo-current under illumination
- Discharged without illumination

Combined power harvesting and storage



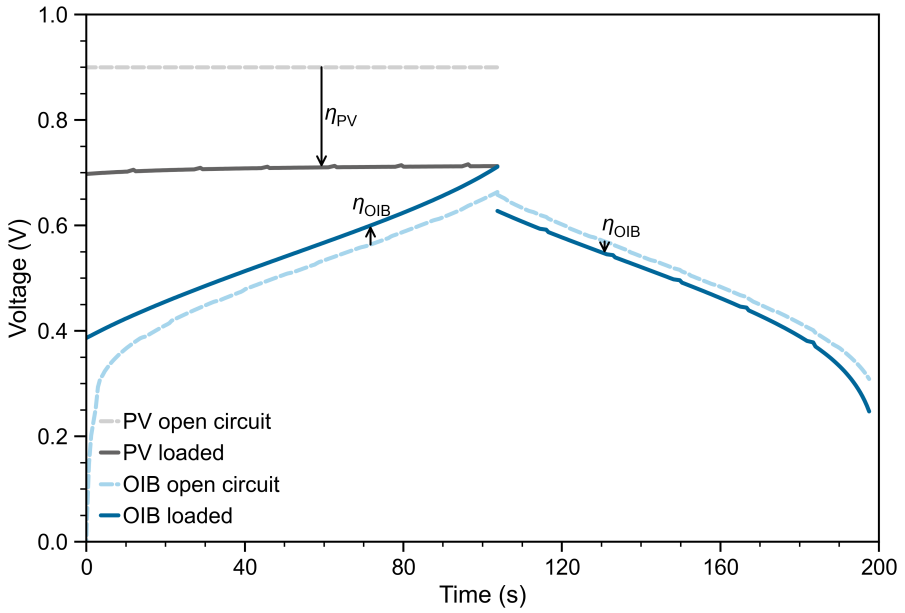
- OIB repeatedly charged with PV
- Discharged without illumination

500 nm LSF, 400 nm LSCrMn, 350 °C, 200 µA cm^{-2} (36 C), 25 Pa O_2, separate cells



500 nm LSF, 400 nm LSCrMn, 350 °C, 200 µA cm^{-2} (36 C), 25 Pa O_2

Harvestore characteristics



- Up to 200 µA cm^{-2} (36 C)
- Up to 10 mJ cm^{-2}
- 86 % energy storage efficiency

500 nm LSF, 400 nm LSCrMn, 350 °C, 200 µA/cm² (20 C), 25 Pa O_2 , separate cells