The Importance of Electrochemistry for the Development of Sustainable Mobility

Jochen Friedl, Ulrich Stimming

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Bridging East and West
Outline

Physical Background/Operating Principle

Outlook/Perspectives

State of the Art
Electrochemical Double Layer Capacitor

![Graph showing energy density and power density of Capacitors, Electrochemical Capacitors (Supercapacitors), Batteries, and Fuel Cells.](image)
Electrochemical Double Layer Capacitor

\[ C_{pf} \approx 1 \text{nF cm}^{-2} \]

\[ C_{DL} = \frac{dQ}{d\phi} \approx 10\mu\text{F cm}^{-2} \]

\[ \phi_{NHE} \approx -4.5 \text{ V vs. vacuum} \]


Electrochemical Double Layer Capacitor

Energy stored in Electrochemical Double Layer (inner & diffuse)

\[ C_{+/-} = \frac{dQ}{dU} \]

\[ C_{act} = \left( \frac{1}{C_+} + \frac{1}{C_-} \right)^{-1} \equiv C \]

\[ E = \frac{1}{2} C U^2 \]

\[ P = \frac{1}{4 ESR} U^2 \]

Electrochemical Double Layer Capacitor

Power Density

\[ U(t) = U_0(1 - \exp\left[-\frac{t}{\tau}\right]) \]

No charge transfer, no reaction:  \( \tau = C \cdot R_s \)

Small \( \tau \)

\( \approx 10 \text{ kW kg}^{-1} \)

Electrochemical Double Layer Capacitor

Energy Density

\[ E = \frac{1}{2} C (1 \, V)^2 \quad \text{aqueous} \]

\[ E = \frac{1}{2} C (2.7 \, V)^2 \quad \text{organic} \]

- High Conductivity
- Electrochemical Stability
- High Surface Area

Carbonaceous material: 5 - 20 \( \mu F \, cm^{-2} \)


Electrochemical Double Layer Capacitor

High conductivity  Electrochemical stability  High surface area

 TEM of typical Disordered Microporous (<2 nm) Carbon
 $S_{\text{BET}} \sim 2000 \text{ m}^2 \text{ g}^{-1}$
 Above $S_{\text{BET}} \sim 1200 \text{ m}^2 \text{ g}^{-1}$
 gravimetric $C_{\text{DL}}$ exhibits plateau.


Electrochemical Double Layer Capacitor

Applications for Mobility:

TOYOTA HYBRID: Hybrid at the Heart of Toyota Racing in 2014 (2014);
Batteries
Batteries
Lead-Acid Battery

\[ E = Q \Delta U \]
\[ E \approx 35 \text{ Wh kg}^{-1} \]

\[ \Delta U = 2.04 \text{ V} \]


Energy stored in Electrodes

\[ \text{Pb}(s) + \text{HSO}_4^- \rightarrow \text{PbSO}_4(s) + H^+ + 2e^- \]

\[ \text{PbO}_2(s) + \text{HSO}_4^- + 3H^+ + 2e^- \rightarrow \text{PbSO}_4(s) + 2H_2O \]
Energy stored in Electrolyte

\[ E = Q \Delta U \]

Redox Flow Batteries

Positive Electrode

Negative Electrode

\[ eU_0^{\text{pos}} = -3.45 \text{ eV vs. vacuum} \]

\[ eU_0^{\text{neg}} = -4.75 \text{ eV vs. vacuum} \]
Batteries
Redox Flow Batteries

\[ E = Q \Delta U \]

\[ \eta = (U - U_0) \]

\[ I = I_0 (\exp \left( \frac{\alpha_a F}{RT} \eta \right) - \exp \left( - \frac{\alpha_c F}{RT} \eta \right) ) \]

18 March 2014
Batteries

\[ E \approx 200 \text{ Wh kg}^{-1} \]

\[ E = Q \Delta U \]

Lithium-Ion Battery

\[ \text{charged} \]

\[ \text{Li}_x \text{C}_6 \rightarrow \text{C}_6 + x\text{Li}^+ + xe^- \]

\[ \text{Li}_{1-x}\text{CoO}_2/\text{Li}_x\text{CoO}_2 \]

\[ \Delta U \approx 3.6 \text{ V} \]

\[ \Delta U \approx 3.7 \]

\[ \text{Li}_x\text{C}_6/\text{C}_6 \]

\[ \approx 0.1 \]
Batteries

**EVA**

**Battery:**
- 170 Wh kg\(^{-1}\)

**Pack:**
- 101 Wh kg\(^{-1}\) 200 Wh kg\(^{-1}\)

United States Advanced Battery Consortium

**Battery Pack:**
- 200 km range in 15 min charging;
- 50 kWh energy content;
- 300 kg battery weight;
- 495 kg pack weight;
- 216 Li-Ion NMC cells;
- 400 V nominal voltage;
- 360 A max. current.

Christian Huber, TUM CREATE
**Batteries**

**Energy Density**

\[ E = Q \Delta U \]

\[ x \text{Li} + M X_y \rightleftharpoons \text{Li}_x M X_y \quad \text{(Insertion)} \]

\[ x \text{Li} + M X_y \rightleftharpoons \text{Li}_x X_y + M \quad \text{(Conversion/Alloying)} \]


Alloying Anode: Silicon

Full Discharge: \( \text{Li}_{22}\text{Si}_5 \rightarrow 4200 \text{ mAh g}^{-1} \) \( \text{LiC}_6 \rightarrow 372 \text{ mAh g}^{-1} \)

Problem: Extreme Volume change \( \rightarrow \) Capacity decay

Possible Approach: Nanostructures with facile strain relaxation

Nanostructured Si anodes are promising, but quantitative understanding is still missing and nature of SEI needs to be understood.

Batteries

Novel Cathode: Li-O₂

Discharge Mechanism: \[ 2 \text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2 \] Up to 1200 mAh g⁻¹

Challenges:

- Electrolyte stability;
- Blockage of porous carbon cathode with discharge products (“clogging”);
- Slow kinetics for charging.

Fuel Cells
Fuel Cells

- Direct conversion of chemical into electrical energy;
- Constant supply of fuel and oxidant.

**Energy Conversion**

\[ j_0^{\text{Pt}} \approx 1\text{ mA cm}^{-2} \]

\[ j_0^{\text{Pt}} \approx 2.8 \times 10^{-4} \text{ mA cm}^{-2} \]

\[ j = j_0 (\exp \left( \frac{\alpha_a nF}{RT} \eta \right) - \exp \left( - \frac{\alpha_c nF}{RT} \eta \right)) \]
Fuel Cells

Complicated reaction mechanism

Hydrogen related reactions:

\[ H_2 + 2 * \leftrightarrow 2 H_{ad} \]

\[ H_2 + * \rightarrow H_{ad} + H^+ + e^- \]

\[ H_{ad} \rightarrow * + H^+ + e^- \]

Tafel
Heyrovsky
Volmer

\[ j_0^{Pt} \approx 1 \text{mA cm}^{-2} \]

Slow kinetics

• Low power;
• High cost.

Increase Temperature.

Model catalyst studies.

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Fuel Cells

Characteristic Curve PEM

Many possible fuels – high energy

kinetic losses evident
POWER: No faradaic reactions
ENERGY: Double layer only
CYCLE LIFE: Very high, no faradaic reaction
POWER: Facile Charge transfer
ENERGY: Stored in electrodes
CYCLE LIFE: Low, electrode conversion
POWER: Sluggish Charge Transfer
ENERGY: Stored in electrolyte
CYCLE LIFE: High, electrodes for charge transfer
POWER: Intercalation reaction
ENERGY: No conversion but intercalation
CYCLE LIFE: High as strain small

![Graph showing power density and energy density对比]
POWER: Very sluggish O₂ reduction
ENERGY: High energy density fuels
Thank you for your attention!