Full State Concentration Estimation for Vanadium Flow Batteries

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Background

VRB concentration estimation is crucial for the battery management system, helping prevent imbalance, gassing reactions, and overcharging, while improving SOC estimation and system efficiency. Using one OCV (Open Circuit Voltages) and two half cell potentials, this work estimates the electrolyte concentrations in the stack and tanks using an Extended Kalman Filter.

VRB Electrode (+/-) Reaction

$$V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+}, \quad E^0 = -0.26\,V$$

$$VO_2{}^+ + 2H^+ + e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} VO^{2+} + H_2O, \quad E^0 = 1\,V$$

Ion Diffusion Reaction

$$V^{2+} + 2V^{5+} \longrightarrow 3V^{4+} \qquad V^{5+} + 2V^{2+} \longrightarrow 3V^{3+}$$

$$V^{3+} + V^{5+} \longrightarrow 2V^{4+} \qquad V^{4+} + V^{2+} \longrightarrow 2V^{3+}$$

$$V^{2+} + V^{4+} \longrightarrow 2V^{3+} \qquad V^{5+} + V^{3+} \longrightarrow 2V^{4+}$$

State Space Model for VRB

$$\frac{V_{stack}}{2}\frac{dc_2^s}{dt} = Q(c_2^t - c_2^s) + \frac{NI}{zF} - N\frac{k_2}{d}c_2^s S - 2N\frac{k_5}{d}c_5^s S - N\frac{k_4}{d}c_4^s S$$

$$\frac{V_{stack}}{2}\frac{dc_3^s}{dt} = Q(c_3^t - c_3^s) - \frac{NI}{zF} - N\frac{k_3}{d}c_3^s S + 3N\frac{k_5}{d}c_5^s S + 2N\frac{k_4}{d}c_4^s S$$

$$\frac{V_{stack}}{2}\frac{dc_4^s}{dt} = Q(c_4^t - c_4^s) - \frac{NI}{zF} - N\frac{k_4}{d}c_4^s S + 3N\frac{k_2}{d}c_2^s S + 2N\frac{k_3}{d}c_3^s S$$

$$\frac{V_{stack}}{2}\frac{dc_5^s}{dt} = Q(c_5^t - c_5^s) + \frac{NI}{zF} - N\frac{k_5}{d}c_5^s S - 2N\frac{k_2}{d}c_2^s S - N\frac{k_3}{d}c_3^s S$$

$$V_n\frac{dc_2^t}{dt} = Q(c_2^s - c_2^t)$$

$$V_n\frac{dc_3^t}{dt} = Q(c_3^s - c_3^t)$$

$$V_p\frac{dc_4^t}{dt} = Q(c_4^s - c_4^t)$$

$$V_p\frac{dc_5^t}{dt} = Q(c_5^s - c_5^t)$$

Discretized model:

$$x_{k+1} = f(x_k, u_k)$$

where $x = [c_2^s, c_3^s, c_4^s, c_5^s, c_2^t, c_3^t, c_4^t, c_5^t]^\top$, $u = [I, Q]^\top$.

Jacobian matrices: $A = \frac{\partial f}{\partial x}$, $B = \frac{\partial f}{\partial u}$

Measurements

Stack Inlet: two half-cell potentials

$$E_{pos} = E^0_{pos} + \frac{RT}{nF}\ln\left(\frac{[VO_2^+]}{[VO^{2+}]}\right)$$

$$E_{neg} = E^0_{neg} + \frac{RT}{nF}\ln\left(\frac{[V^{3+}]}{[V^{2+}]}\right)$$

Stack Outlet: one OCV

$$E_{cell} = E_{pos} + E_{neg}$$

$$y_k = [E_{pos,k}, E_{neg,k}, E_{cell,k}]^\top$$

Jacobian matrix $H = \frac{\partial y}{\partial x}$

Extended Kalman Filter

Algorithm 1 Predict the State using the Discretized Model

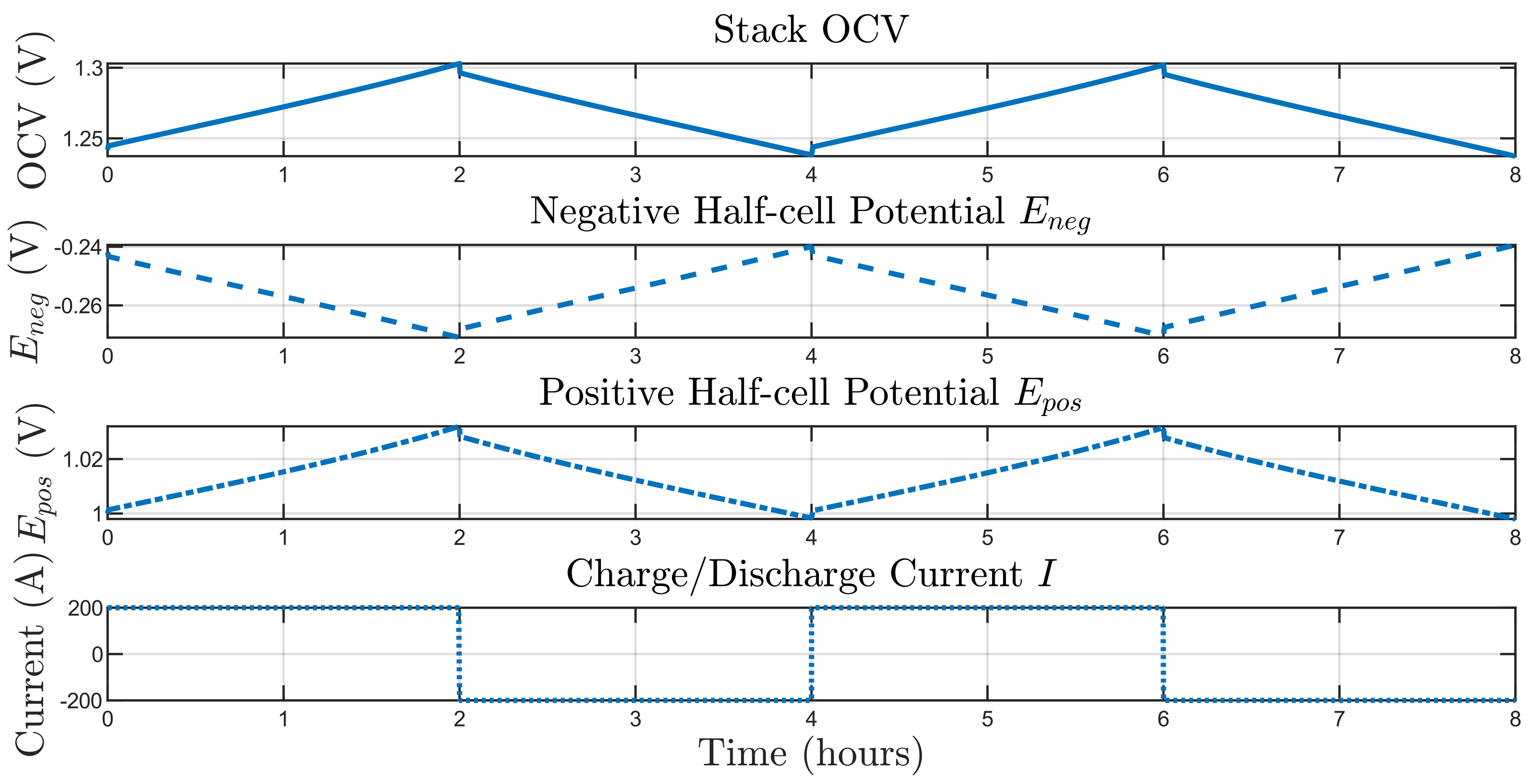
Initialization:
Set the initial state estimate $\hat{x}_0$
Set the initial error covariance P_0
for each time step k **do**
  Prediction Step:
  Predict the state: Use $x_{k+1} = f(x_k, u_k)$ to get $\hat{x}_{k|k-1}$
  Predict the error covariance: $P_{k|k-1} = AP_{k-1}A^T + Q$
  Update Step:
  Compute the Kalman Gain: $K_k = P_{k|k-1}H^T(HP_{k|k-1}H^T + R)^{-1}$
  Compute the residual: $residual = y_k - H\hat{x}_{k|k-1}$
  Update the state estimate: $\hat{x}_k = \hat{x}_{k|k-1} + K_k(y_k - H\hat{x}_{k|k-1})$
  Update the error covariance: $P_k = (I - K_kH)P_{k|k-1}$
end for

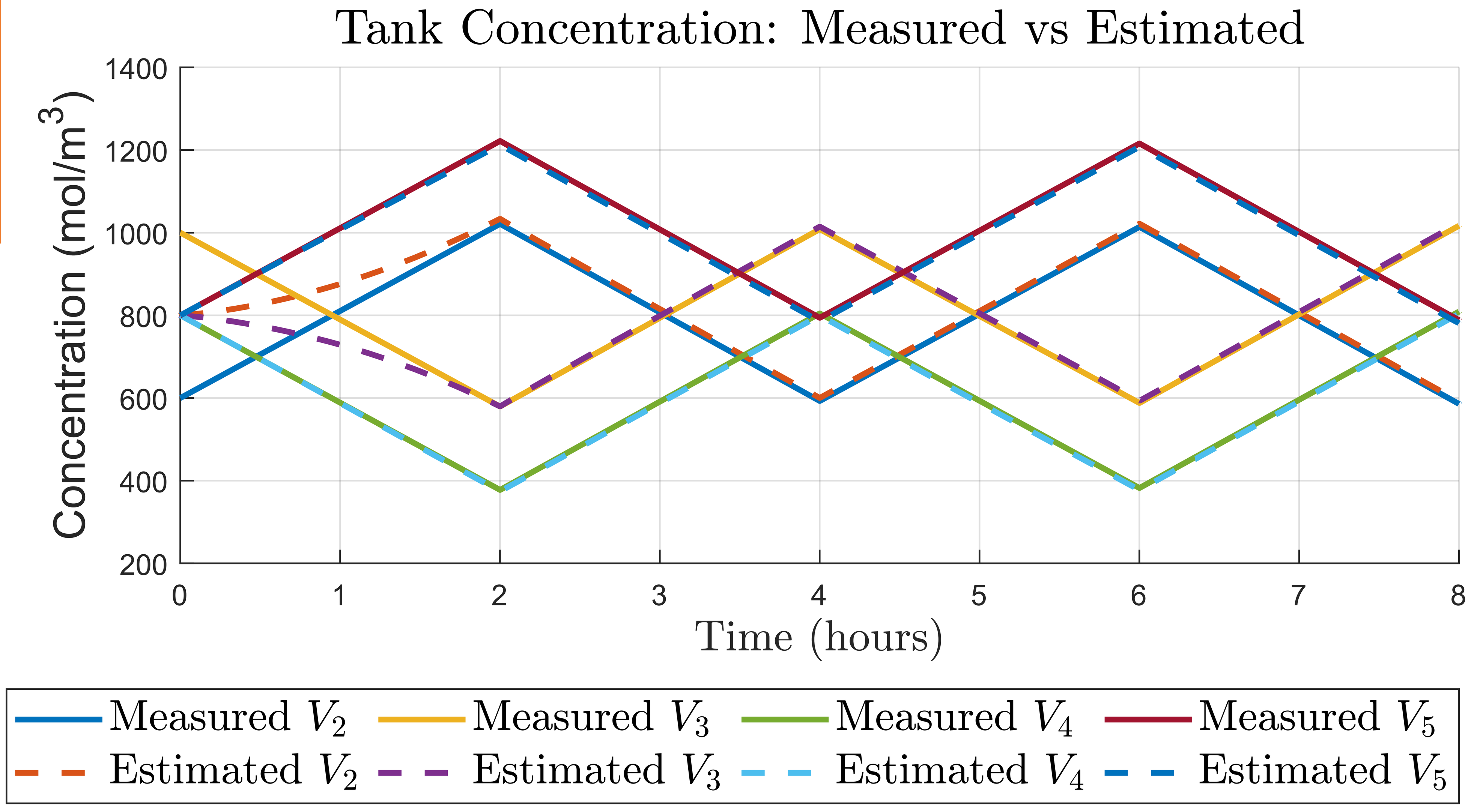
Significance

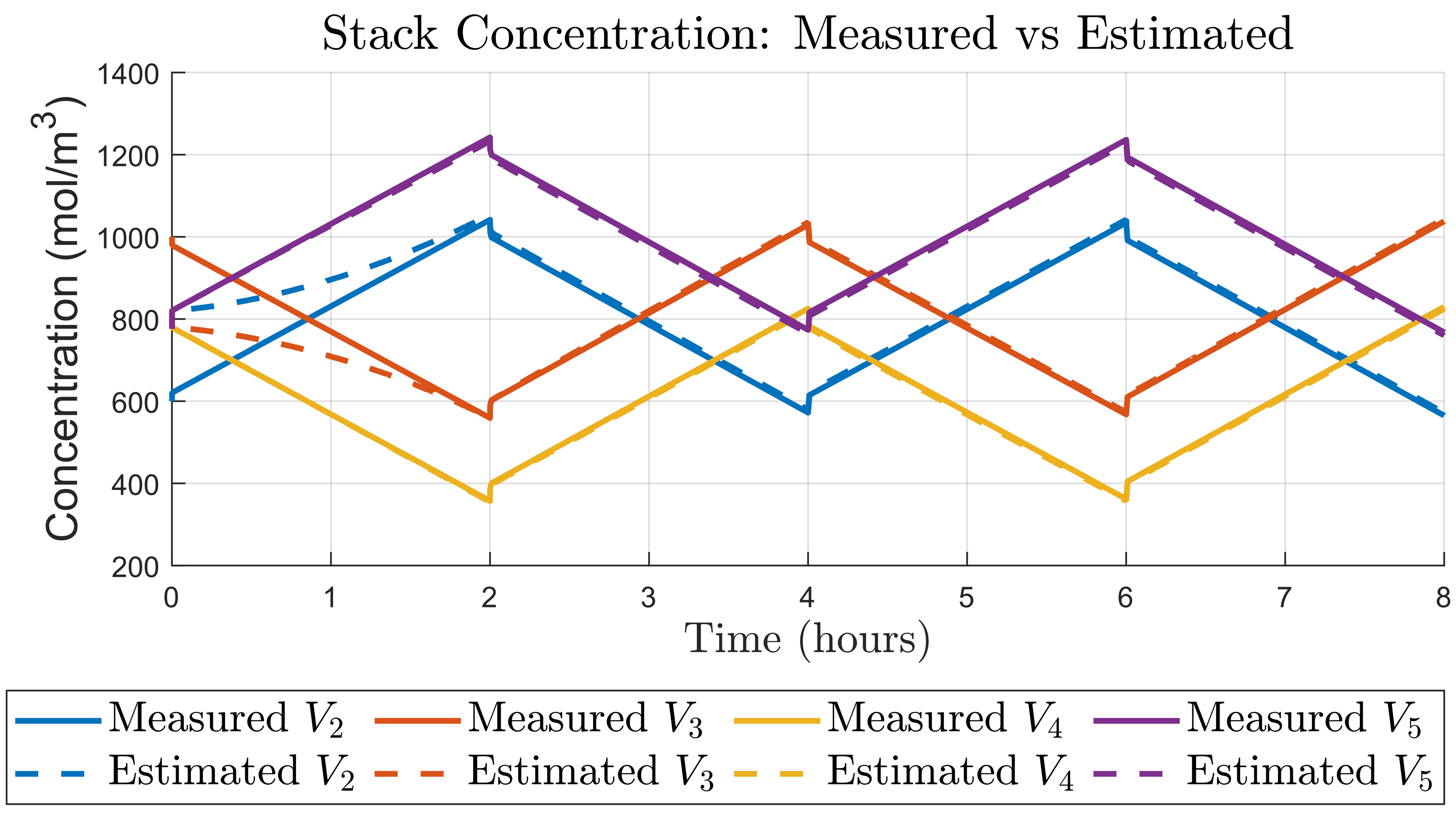
- Avoid gassing reaction
- Estimate electrolyte imbalance
- Accurate SOC estimation
- Fault detection

Simulation Results

Parameters	Values
Overall Electrolyte Concentration	1.6M/L
Number of Cells	200
Tank Volume +	$7\,m^3$
Tank Volume -	$7\,m^3$
$\boldsymbol{Q}$	0.1I
$\boldsymbol{R}$	$\text{diag}(1e^{-3}, 1e^{-3}, 1e^{-3})$
$\boldsymbol{P_0}$	$100\boldsymbol{I}$







Conclusion and Future Work

A full state Extended Kalman Filter has been developed to estimate ion concentrations of VRBs in the stack and tanks. Future studies will include real-time detection of abnormal conditions during battery operation for improved reliability and operational performance.

Refs: Tang, A. (2014). *Dynamic modelling and simulation of the all-vanadium redox flow battery* (Doctoral dissertation, UNSW Sydney).
Simon, D. *Optimal State Estimation: Kalman, H Infinity, and Nonlinear Approaches*. John Wiley & Sons, 2006.