Title of Abstract	Optimal Charging of Nickel-Hydrogen Batteries for Life Extension
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Please enter short abstract

We are exploring the possibility of extending the cycle life of battery systems by using a charging profile that minimizes cell damage. Only nickel-hydrogen cells are discussed at this time, but applications to lithium-ion cells are being considered. The process first requires the development of a fractional calculus based nonlinear dynamic model of the specific cells being used. The parameters of this model are determined from the cell transient responses. To extend cell cycle life, an instantaneous damage rate model is developed. The model is based on cycle life data and is highly dependent on cell voltage. Once both the cell dynamic model and the instantaneous damage rate model have been determined, the charging profile for a specific cell is determined by numerical optimization. Results concerning the percentage life extension for different charging strategies are presented. The overall procedure is readily adaptable to real-time implementations where the charging profile can maintain its minimum damage nature as the specific cell ages.

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Optimal Battery Charging for Damage Mitigation

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Electrical and Computer Engineering

Control Philosophy

Two Phases of Control System Design:

Phase I is the design of optimal trajectories and associated inputs, that move a given plant from one operating condition to another, while minimizing some performance measure. Requires a nonlinear dynamic model of the specific system.

Phase II is the design of a trajectory following controller (sometimes called a regulator or tracker) that provides a real-time control input perturbation to keep the plant operating near the designed optimal trajectory. Usually uses a linearized dynamic model of the specific system.

Phase I:
Our control philosophy is to charge the NiH2 cell in such a way that the damage incurred during the charging period is minimized, thus extending its cycle life. Requires nonlinear dynamic model of NiH2 cell and a damage rate model. We must do this first.
This control philosophy is generally considered damage mitigating control or life-extending control.

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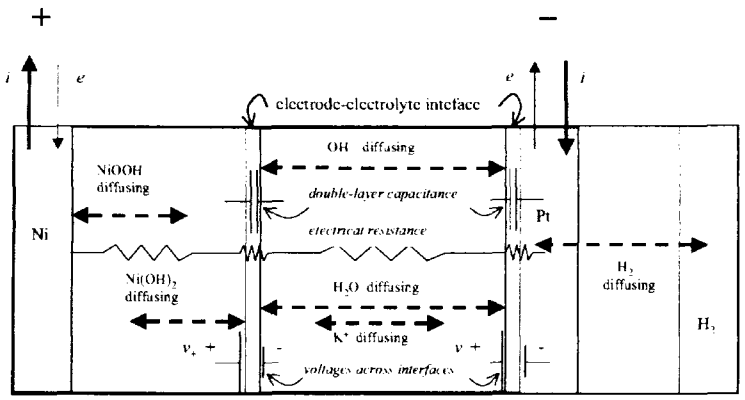
Overview of NiH2 Electrochemistry



Normal charge-discharge operation of a nickel-hydrogen cell:

positive nickel electrode: $NiOOH + H_2O + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Ni(OH)_2 + OH^-$

negative hydrogen electrode: $\frac{1}{2} H_2 + OH^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} H_2O + e^-$.

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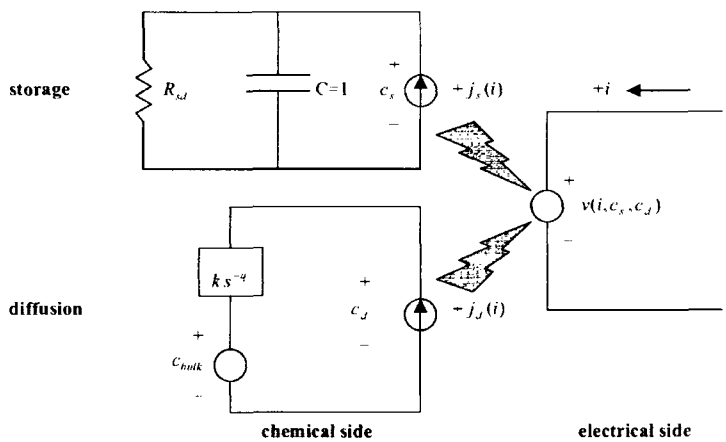
Essentialized performance model of NiH2 cell.



$S + D + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}}$ reaction products

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Electrode Behavior: Faraday's Law

- For the discussion of the next two sections, consider the electrode process :

$$aA + bB \longleftrightarrow cC + dD + ne^{-}.$$

- This equation represents both a chemical process and an electrical process.
- The reaction rates can be completely determined using the electrical process by seeing that the chemical conversion can only occur if electrons are either arriving or leaving.
- Thus, the chemical conversion rates are controlled by, or measured by, the electrical current passing through a given electrode.
- Then recognizing that the rate of electron production is related to electrical current *i*, the following rate equations result :

$$-i \equiv \frac{dq_{e^-}}{dt} = -\frac{d}{n}\frac{dD}{dt} = -\frac{c}{n}\frac{dC}{dt} = +\frac{a}{n}\frac{dA}{dt} = +\frac{b}{n}\frac{dB}{dt}$$

where q_{e^-} is the charge of a single electron.

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Electrode Behavior: Electrode Equation

Consider the fluxes, *j*, of the species in the forward and reverse reactions at the electrode,

$$i = j_f - j_r.$$

Assuming that the species fluxes are proportional to concentrations, yields

$$i = k_f c_A^a c_B^b - k_r c_C^c c_D^d.$$

The rate constants, *k*, can be related to the electrical potential across the electrode-electrolyte interface using free energy considerations,

$$k_f = k_0 e^{(F/RT)(1-\alpha)(v-v_0)}$$
$$k_r = k_0 e^{(F/RT)(-\alpha)(v-v_0)}$$

Inserting these gives the electrode equation,

$$i = k_0\left(c_A^a c_B^b\, e^{(F/RT)(1-\alpha)(v-v_0)} - c_C^c c_D^d\, e^{(F/RT)(-\alpha)(v-v_0)}\right).$$

The approach used is often referred to as the Butler-Volmer approach.

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Linear-in-the-parameters Electrode Equation

We propose a linear-in-the-parameters approximate solution to the electrode equation;

$$v = k_1 + k_2 \ln(1 + |i|)\mathrm{sgn}(i) + k_3 \ln(c_d) + k_4 \ln(1 - c_s)$$

where the *k*'s are parameters to be determined from data.

This represents a compromise between the Tafel and the Nernst solutions of the electrode equation:

The Nernst solution assumes that the current is so small as to be negligible

$$v = v_0 + \frac{RT}{nF} \ln\left(\frac{c_s}{c_d}\right).$$

The Tafel solution assumes that the current is large in one direction or the other, which means that one of the two exponential terms is negligible

$$v = v_0 + \frac{RT}{\alpha nF} \ln(k_0) - \frac{RT}{\alpha nF} \ln(i).$$

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Essentialized Model Overview

Terminal behavior: **current into the battery is +*i*,**
the terminal voltage is +*v*,

stored material with self-discharge:

$$\frac{dc_s(t)}{dt} = i(t) - \frac{1}{R_{sd}} c_s(t),$$

diffusing material:

$$c_d(t) = c_{bulk} - k_d \, {}_0d_t^{-q} i(t),$$

electrode-equation:

$$v(c_s, c_d, i) = k_1 + k_2 \ln(1 + |i|)\mathrm{sgn}(i) + k_3 \ln(c_d) + k_4 \ln(1 - c_s).$$

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Parameter Determination

The cell chosen is the NSWC Crane Pack ID 3602G (Gates):

rated at 65 AHr
uses 31% KOH concentration
maintained at 10 degrees C
charge-discharge profile is a square wave
with 35% depth-of-discharge (DOD)
104% recharge ratio
current is 26.29 A for 54 minutes charging
–37.92 A for 36 minutes during discharge
note that 65 AHr = 3900 AMin, 35% of 65 AHr = 1365.1 AMin .

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Essentialized Model with Identified Parameters

Terminal behavior: **current into the battery is +*i*,**
the terminal voltage is +*v*,

stored material with self-discharge:

$$\frac{dc_s(t)}{dt} = i(t) - 0.0002085c_s(t),$$

diffusing material:

$$c_d(t) = 1 - 0.001036_0 d_t^{-0.9034} i(t),$$

electrode-equation:

$$v = 1.3656 + 0.0265\ln(1+|i|)\mathrm{sgn}(i) + 0.0229\ln(c_d) - 0.0262\ln((1.005*3900 - c_s)/3900)$$

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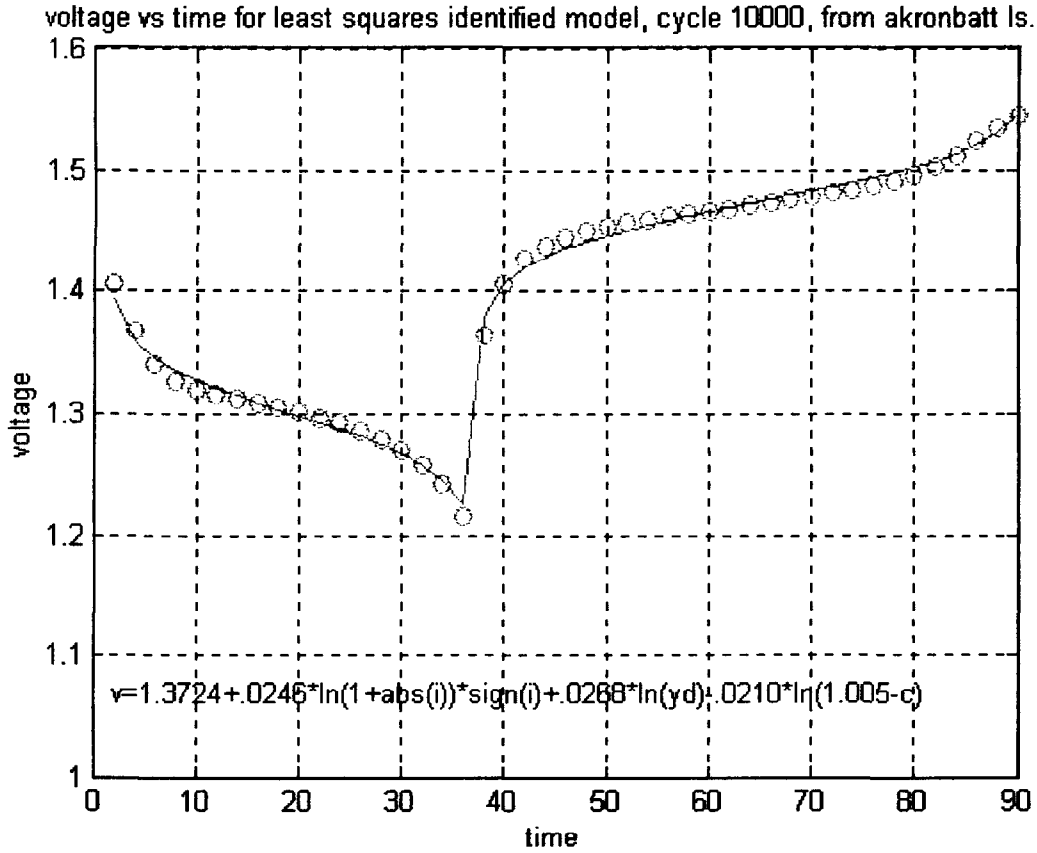
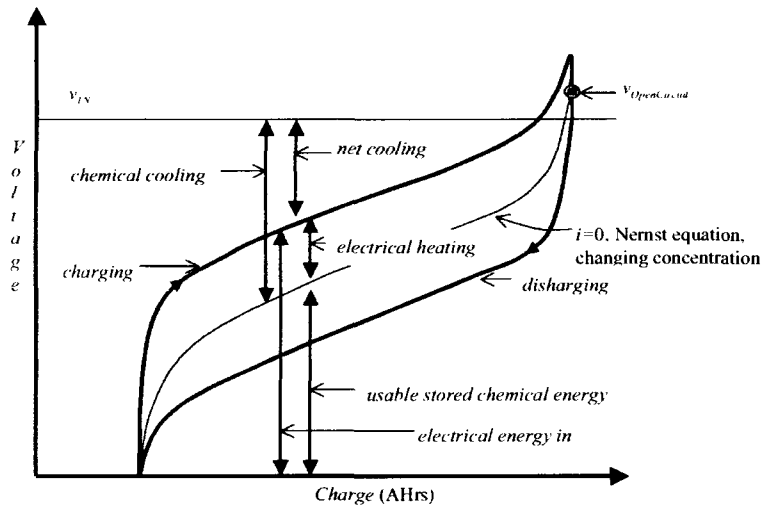


A typical charge-discharge cycle, charging.



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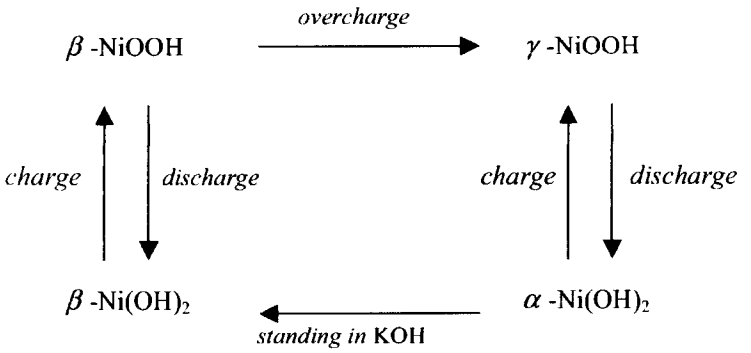
Damage Mechanisms for NiH2 Batteries

Formation of γ- phase NiOOH:



Bode's Solid phase relationships for a NiOOH electrode.

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Damage Mechanisms for NiH2 Batteries

Formation of O2:

Overcharge: 1) continuing to charge the cell after all the β-$Ni(OH)_2$ has been converted
2) the charging current is too large

The effect of this is the formation of O_2 at the nickel electrode, along with heating.

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Damage Mechanisms for NiH2 Batteries

Heating:

Sources: 1) heat of reaction
2) formation of O_2
3) electrical current

Results in: 1) the formation of γ-NiOOH:
which a) reduces cell capacity
b) does physical damage to the cell

Results in an increase in self-discharge reaction rates.

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Battery Continuum Damage Modeling

- **Many Possible Damage Mechanisms**
  - **Hard to model all these**
- **Overall Birth to Death Data will be Used Instead**
- **Crane Database Provides much Information**
- **Green-Hoffman Data Taken as Starting Point**

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Battery Continuum Damage Modeling

Green-Hoffman Data NiH_2 at $T = 10\ ^{o}C$

DOD	Cycles To Failure
35%	38,000
50%	19,000

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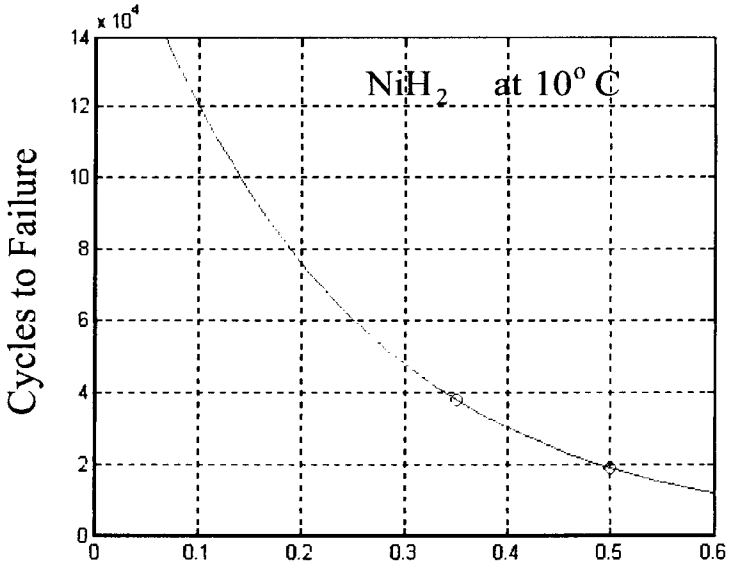
Green-Hoffman Battery Life Model



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Continuum Damage Model

Based on G-H Data

$$N_{f_{GH}} = 1885.04 e^{4.621(1-DOD)}$$

$$= 191511.73 e^{-4.621 DOD}, \quad \text{at } 10^{\circ}\text{C}$$

For constant damage per cycle

$$D_{cyc} = \frac{1}{N_{f_{GH}}} = 5.222 \times 10^{-6} e^{4.621\, DOD}$$

$$DOD = c_1 v_a$$

$$D_{cyc} = 5.222 \times 10^{-6} e^{4.621 c_1 v_a}$$

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Continuum Damage Model

$$\int_{cycle} \hat{\delta}(v)\, dv = D_{cyc} = 5.222 \times 10^{-6} e^{4.621 c_1 v_a}$$

where $\hat{\delta}(v) = \frac{dD}{dv}$ = voltage referred damage rate

For damage on charging only

$$\int_{v_{\min}}^{v_{\max}} \hat{\delta}(v)\, dv = D_{cyc} = 5.222 \times 10^{-6} e^{4.621 c_1 v_a}$$

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Continuum Damage Model

$$\int_0^{v_{\max}-v_{\min}} \hat{\delta}(v+v_{\min})\,dv = 5.222\times10^{-6} e^{4.621 c_1 v_a}$$

$$= 5.222\times10^{-6} e^{4.621 c_1 (v_{\max}-v_{\min})}$$

Thus inferring

$$\hat{\delta}(v+v_{\min}) \cong 5.222\times10^{-6}\, 4.621\, c_1\, e^{4.621 c_1 v}$$

$$= 2.4131\times10^{-5} c_1\, e^{4.621 c_1 v}$$

Hence

$$\hat{\delta}(v) = 2.4131\times10^{-5} c_1\, e^{4.621 c_1 (v-v_{\min})}$$

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Continuum Damage Model

Instantaneous Damage Rate

$$\dot{D}(t) \equiv \frac{dD}{dt} = \frac{dD}{dv}\frac{dv}{dt} = \hat{\delta}(v(t))\,\dot{v}(t)$$

Requiring Positive Damage

$$\dot{D}(t) \equiv \frac{dD}{dt} = \frac{dD}{dv}\left|\frac{dv}{dt}\right| = \hat{\delta}(v(t))\,|\dot{v}(t)|$$

$$\dot{D}(t) = 2.4131\times10^{-5} c_1\, e^{4.621\, c_1 (v-v_{\min})}\,|\dot{v}(t)|$$

$$\dot{D}(t) = 2.4131\times10^{-5} c_1\, e^{4.621\, c_1 (v-1.2)}\,|\dot{v}(t)|$$

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Modified Continuum Damage Model

For zero damage at zero DOD

$$D_{cyc} = c_2\left(e^{c_3 DOD} - e^{c_3 0}\right)$$

$$D_{cyc} = c_2\left(e^{c_3 DOD} - 1\right) = \frac{1}{N_f}$$

c_2 and c_3 are determined to match G-H Data

$$D_{cyc} = 1.0404\times10^{-5}\left(e^{3.602\,DOD} - 1\right) = \frac{1}{N_f}$$

Repeating the previous process gives

$$\dot{D}(t) = 3.7475\times10^{-4} c_1 e^{3.602\,c_1(v-1.2)}\left|\dot{v}(t)\right|$$

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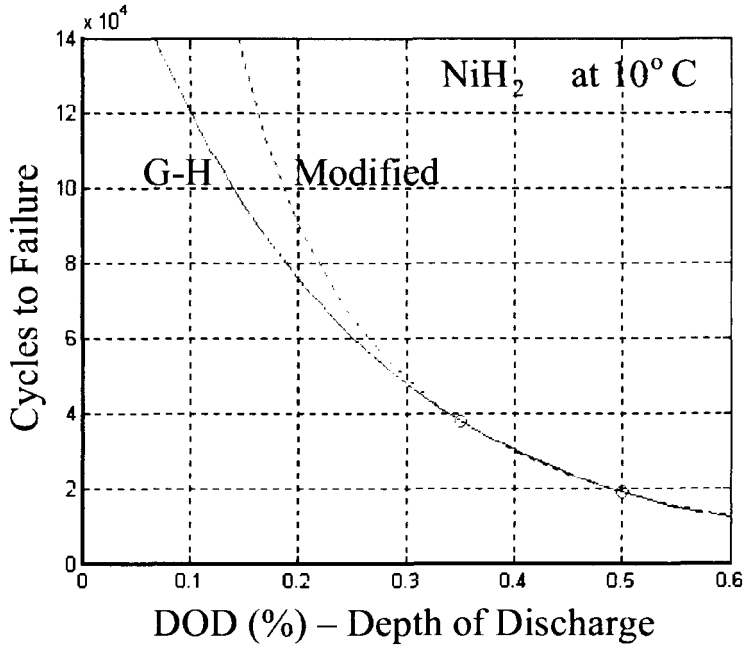
Battery Life Models



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Modified Continuum Damage Model

In terms of current

$$\dot{D}(t) \equiv \frac{dD}{dt} = \frac{dD}{dv}\left|\frac{dv}{dq}\right|\left|\frac{dq}{dt}\right| = \hat{\delta}(v(t))\left|\frac{dv}{dq}\right| |i(t)|$$

where $\frac{dv}{dq}$ is slope of charging curve

For zero damage when voltage rate goes negative

$$\dot{D}(t) = 3.7475\times10^{-4}\, c_1\, e^{3.602 c_1 (v-1.2)}\, \dot{v}(t), \quad \dot{v}(t) \geq 0$$
$$\dot{D}(t) = 0, \quad \dot{v}(t) < 0$$

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Control Philosophy

Two Phases of Control System Design:

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Performance Measure

The **performance measure** to be minimized is the accumulated damage per recharge cycle:

$$J = w_{fs}\left(c_s^*(t_f) - c_s(t_f)\right)^2 + \int_0^{t_f} \frac{dD(t)}{dt}\,dt$$

$c_s^*(t_f)$ is the desired stored charge at the end of charge,

w_{fs} is the cost weighting ,

$\frac{dD(t)}{dt}$ is obtained from the damage model,

t_f for our problem is 54 Min.

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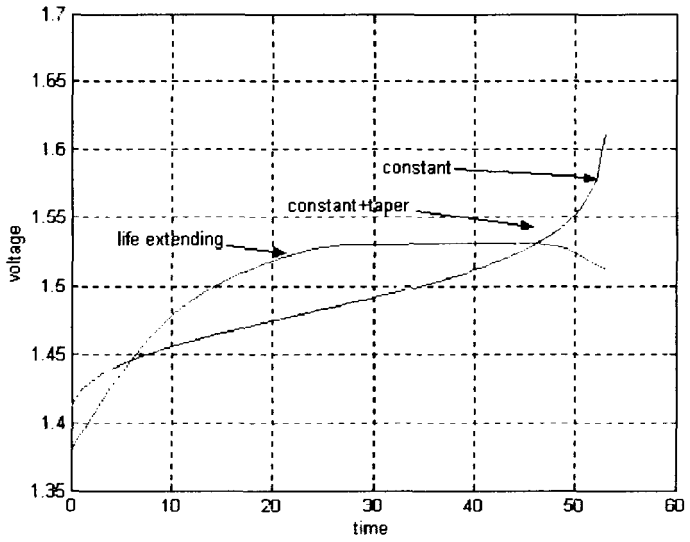
65%-100% recharging, voltage profile



Comparison of 65%-100% charging methods, voltage

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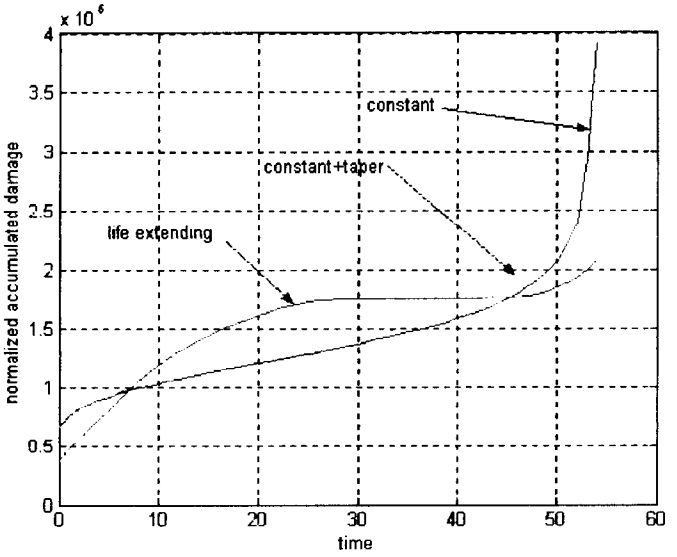
65%-100% recharging, damage profile



Comparison of 65%-100% charging methods, damage.

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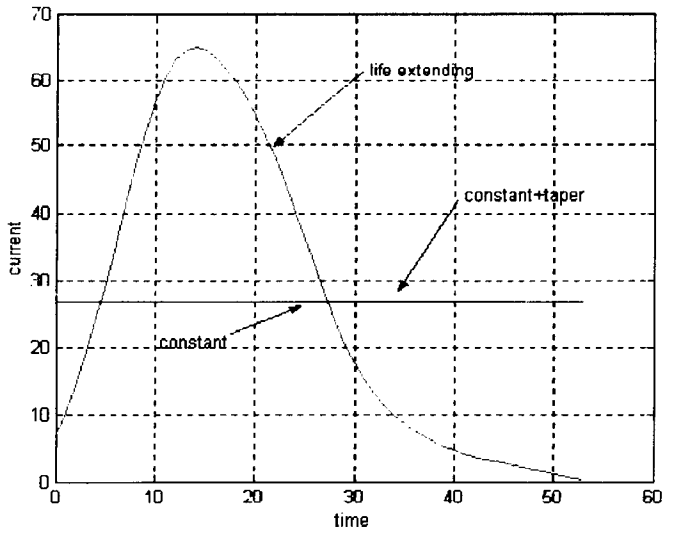
65%-100% recharging, current profile



Comparison of 65%-100% charging methods, current.

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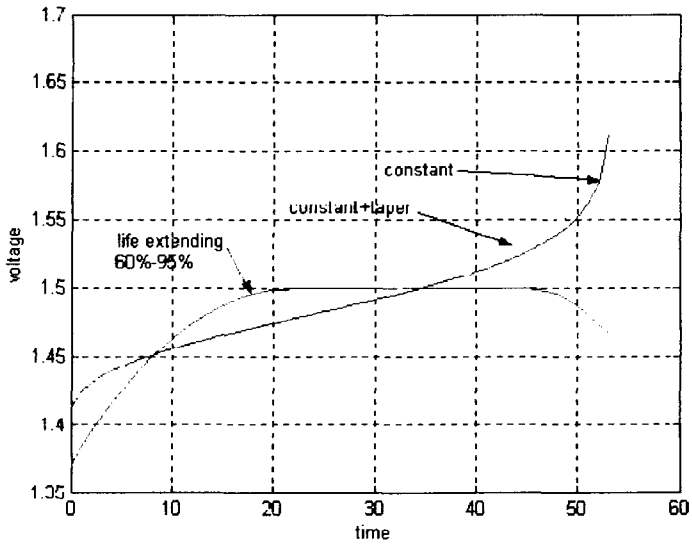
60%-95% recharging, voltage profile



Comparison of 60%-95% and standard charging methods, voltage.

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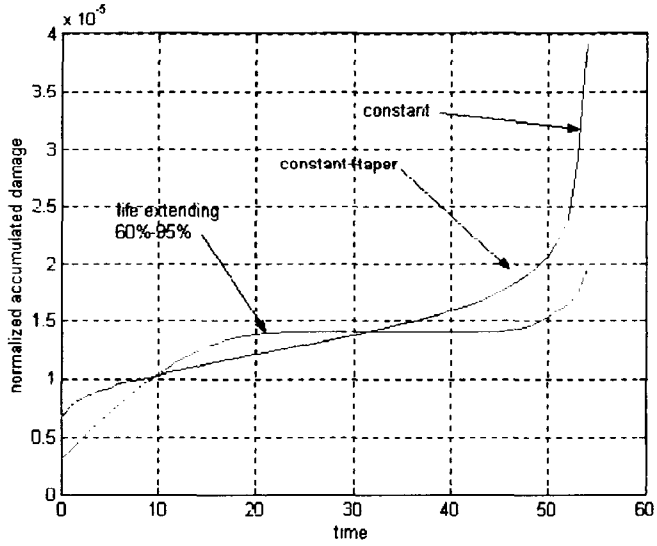
60%-95% recharging, damage profile



Comparison of 60%-95% and standard charging methods, damage.

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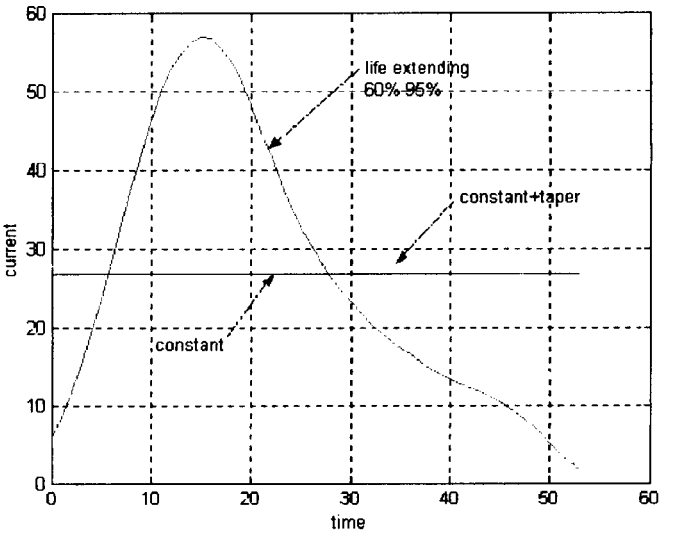
60%-95% recharging, current profile



Comparison of 60%-95% and standard charging methods, current.

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Optimal Charging Summary

	Damage per Cycle	Cycles to Failure	% Life Extension relative to constant current	% Life Extension relative to constant current-plus-taper
Constant-Current Charging	0.000039269	25465	0%	not applicable
Constant + Taper Charging	0.000026316	38000	49.22%	0%
Life Extending Charging 65%-100% Cycle of Figure 5.4 with abs(dv/dt) damage rate	0.000020780	48123	88.98%	26.64%
Life Extending Charging 60%-95% Cycle of Figure 5.5 with abs(dv/dt) damage rate	0.000019535	51190	101.02%	34.71%
Life Extending Charging 65%-100% Cycle of Figure 5.6 with only +dv/dt damage rate	0.000022080	45290	77.85%	19.18%

Comparison of damage for various charging methods, assumes damage only during charge. Percentage life extension is reduced proportionately for damage during discharge.

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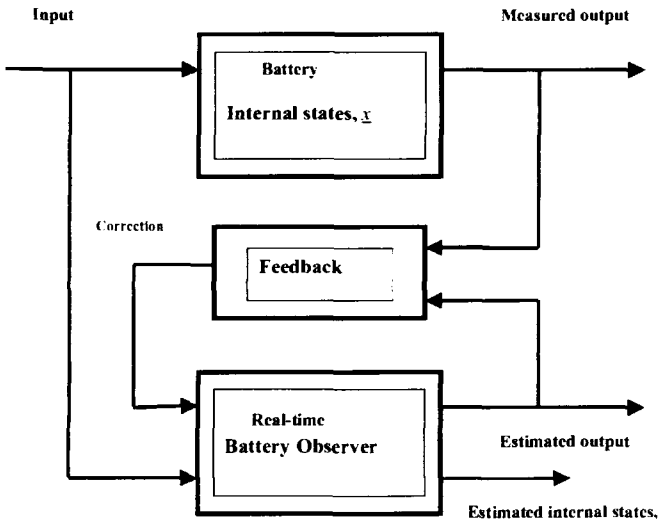
Control Design - Phase II: Tracking



Real-time observer structure.

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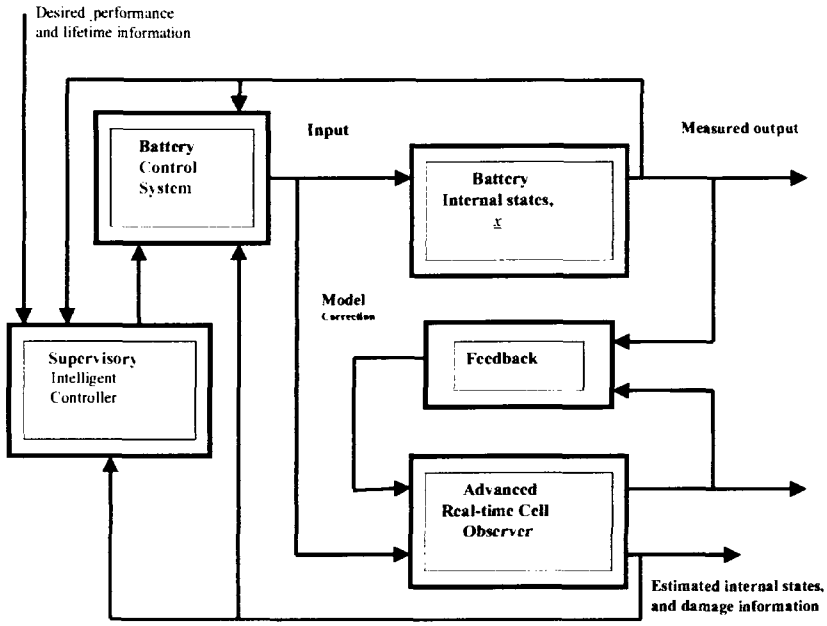
Control Design - Phase II: Tracking



Advanced control system using advanced real-time observer.

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Summary

- **Control Philosophy**
- **Essentialized Model Development**
- **Damage Model**
- **Optimal Life-Extending Charging**
- **Tracking Controller**
- **Real-time Parameter Identification Development**
- **Application to Lithium based cells**

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