정·부극 재료의 특성에 따른 리튬이온전지의 용량설계

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Capacity Design of Lithium Ion Battery Based on the Characteristics of Materials

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Abstract

In order to design capacity of lithium ion battery, some calculations were carried out based on the characteristics of materials by the given battery shape and dimension. The principle of design was built by the interpretation of the correlation of material, electrochemical and battery factors. Parameters of materials are fundamental physical properties of constituent such as cathode, separator, anode, current collectors and electrolyte. Electrochemical factor includes potential pattern as a function of specific capacity, specific discharge capacity(or initial irreversible specific capacity or Ah efficiency) as a function of specific charge capacity and material balancing. Parameters of battery are dimension, construction hardware and performance.

Battery capacity was simulated for a lithium cobalt dioxide as cathode and a hard carbon as anode to achieve 1100 mAh for the charge limit voltage of 4.2V, the weight ratio(+/-) of 2.4 and ICR18650. A fabricated test cell(ICR18650) which have weight ratio(+/-) of 2.4 discharged to 1093 mAh for the charge limit voltage of 4.2V. The sequential discharge capacity show good correspondence with designed capacity.

Acknowledgement

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목 차

I. 개요

□ ***전지용량설계 측면의 리튬이온전지***
- Intercalation Chemistry를 사용하는 전지
- 정극재료, 부극재료 및 전해액에 따라 각기 다른 리튬이온전지
- 충방전 중 정극과 부극의 전위가 각각 변함
- 정교하게 Material Balancing된 전지설계 필요

□ ***기존 리튬전지 설계기술***

리튬금속부극 리튬1차전지에 대한 Computer Aided Design
; N. Marincic (1975년)

□ ***리튬이온전지와 리튬1차전지의 용량설계상 차이점***

; 리튬금속부극을 탄소부극으로 대체
- 리튬금속부극 - 충·방전 시 전위변화 적음
  - 전지전압변화 - 정극재료의 전위변화에 대한 함수
- 탄소부극 채용 리튬이온전지
  ; 충·방전 중 정극과 부극의 전위가 동시에 변화

□ ***리튬이온전지 설계법 개발의 난점***

; 전지전압 - 정극 및 부극 전위변화의 복합 함수
- 정·부극 material balance의 factor가 다양

※ 리튬이온전지의 설계법이 일반화되지 못함

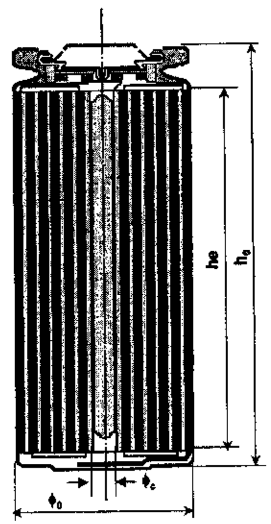
□ ***리튬이온전지 설계법 관련 연구 현황***
- 기본특성(재료 및 전지성능 등) 연구 진행
- 각 세부항목의 상관성과 설계원칙의 일반화 연구 저조
- 본 연구에서 리튬이온전지의 용량설계기술 연구 소개
  ; 기준 전지조건에서의 전지용량설계 해석

□ ***개발 기술의 활용***
- 리튬이온전지 기술 중 전지설계 기술 제공
  ; 효율적 기술개발 유도
- LPB 등 타 전지의 전지설계법 개발에 활용

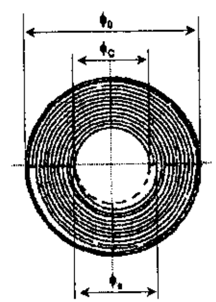
II. 리튬이온전지의 형태

설계기준전지 : ICR18650 Jelly Roll Cylindrical Battery

Cross-sectional View of Jelly Roll LIB



(a) side view



(b) top view

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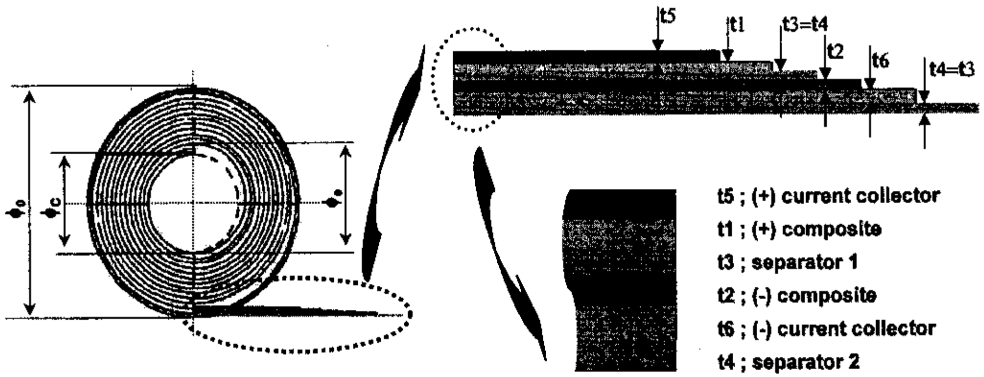
Top View and Fine Illustration of Jelly Roll Winding in LIB



(a) top view of winding (b) unit cell layer stacking

III. 전지설계 특성인자

□ ***전지성능 영향인자***

; 재료 factor ; 전기화학적 factor ; 전지외형 factor

① Material Factor

; 정/부극, 집전체 및 격리막의 두께, 다공도, 밀도 및 길이

; 전해액의 조성, 밀도, 전도도 및 함량

② Electrochemical Factor

; 정/부극의 활물질 함량, 임피던스, 쿨롱효율 및 비용량

; 정/부극의 material balance을 위한 유효 정/부극 Utilization

③ Battery Factor

; 전지에 따른 Roll의 내경, 외경 및 높이의 형태

; Jelly Roll 제조시 구성물(정/부극 및 격리막)의 Sliding의 규격화

□ ***전지성능 영향인자 세부사항***

① Material Factors

Components	Design Parameters
Cathode	Thickness; Specific capacity; Coulombic efficiency; Length; Height; Apparent density; Active material content; Material density; Porosity
Separator-I	Type; Thickness; Porosity; Density; Length exact; Length; Height
Anode	Thickness; Specific Capacity; Coulombic Efficiency; Length; Height; Apparent Density; Active material content; Material Density; Porosity
Separator-II	Type; Thickness; Porosity; Density; Length; Height
(+) Current Collector	Material; Density; Thickness; Conductivity; Length; Height
(-) Current Collector	Material; Density; Thickness; Conductivity; Length; Height
Electrolyte	Composition; Density; Conductivity

② Electrochemical Factors

Components	Design Parameters
Electrode Performance	Cathode volume; Efficiency; Specific cathode charge capacity; Effective specific cathode capacity; Cathode mixture weight; Cathode weight; Anode volume; Efficiency. Specific Anode Charge Capacity; Effective specific anode capacity; Anode mixture weight; Anode weight; Separator volume; Separator weight; Cathode current collector volume; Cathode current collector weight; Anode current collector volume; Anode current collector weight; Electrolyte volume; Electrolyte weight; -/+ capacity ratio; +/- weight ratio (Rw)

③ Battery Factors

Components	Design Parameters
Battery Dimension	Type; Height; Diameter; Weight; Volume; Effective height; Effective diameter; Core diameter; Number of winding; Battery capacity; Core+Separator diameter
Unit Volume Parameters	Effective Design Volume; Calculated volume; Effective capacity density; Unit stack thickness
Construction body	Weight (mandrel, tab, top cap, gasket, can 등)
Basic Battery Performance	Chode voltage; Charge cathode potential; Charge anode potential; Discharge voltage; Discharge cathode potential; Discharge anode potential; Resistance of specific volume

IV. 전지특성 영향인자간의 관련성

ㅁ *관련성 해석 항목*

- o 설계 원칙/인자의 설정 및 인자간의 관련성 해석
- o 전지설계 특성인자간의 상호관련성 해석
- o 높이/길이/폭 등 dimension 해석
- o material balance에 기초한 전압/비용량 해석
- o 기준 dimension에 대한 전지용량 해석

ㅁ *Jelly Roll Winding에 따른 Sliding Pattern 해석*

o 구성품 : 정극, 부극, 격리막(1), 격리막(2)

$$L1 = t_0\pi n^2 + \phi_{cs}\pi n \quad (1)$$

$$L2 = L1 + 2t_1\pi n \quad (2)$$

$$L3 = L2 + 2t_2\pi n \quad (3)$$

$$L4 = L3 + 2t_3\pi n \quad (4)$$

$$t_1 = \frac{Q}{q_{01}d_1L_1h_1(1-P_1)} + t_{cs} \quad (5)$$

$$t_3 = \frac{QRw}{q_{03}d_3L_3h_3(1-P_3)} + t_{as} \quad (6)$$

$$\phi_1 = \phi_0 - t_0(2n-0.5) \quad (7)$$

$$Q = \phi_0^2\pi\frac{H}{4} \times QD \quad (8)$$

$$t_0 = t_1+t_2+t_3+t_4 = t_1+2t_2+t_3 \quad (9)$$

where

- L1 = length of cathode
- L2 = length of first separator
- L3 = length of anode
- L4 = length of second separator
- t1 = thickness of cathode including current collector
- t3 = thickness of anode including current collector
- t2, t4 = thickness of first and second separator
- t0 = total thickness (electrodes and separators)
- t_{cs} = thickness of cathode separation
- t_{as} = thickness of anode separation
- n = number of turns
- ϕ_{cs} = starting diameter (mandrel+separator)
- ϕ_0 = effective diameter
- QD = effective capacity density
- h1 = height of cathode
- h3 = height of anode
- Q = battery capacity

- Sliding Pattern으로부터 L1, L3, t3, t0, n의 Solution 도출

- 각 전지설계인자를 실험과 계산에 의한 factor로 분류/해석

- 전지용량설계의 Key Parameter는
  - 정·부극재료의 specific capacity 및 Ah efficiency
  - 전지설계 적용을 위한 용량조화(material balance) 필요

V. 용량조화 (Material Balance)

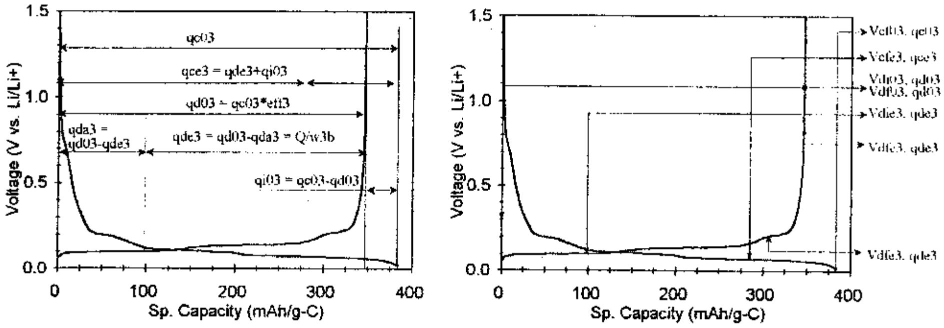
- *Effective Charge Capacity를 설정*
  ; 정·부극의 상호작용으로 결정
  ; 정·부극재료의 전기화학적 고유특성 극대화
  → 고 전지성능 구현

- *재료 고유특성의 극대화*
  ; 전극전압 제어에 기초
  ; 전지/전극의 충전전위설정 필요
  ; 부극(흑연계)의 경우 High dQ/dV
  → 전위제어에 의한 용량설계시 큰 편차
  → 부극충전용량비율 또는 정부극중량비설정 필요

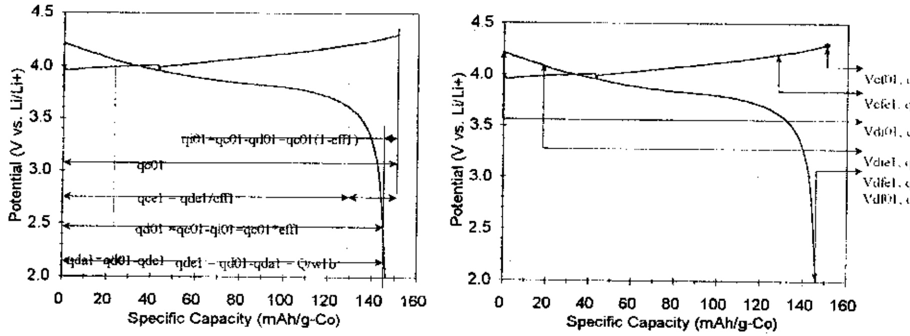
1. 용량조회 변수 설정

Graphical presentation 참조 : 변수의 상세 설명 생략

□ *Potential-Capacity Relationship of Anode*



□ *Potential-Capacity Relationship of Cathode*



2. 용량조회 Factor의 상관 관계

□ *쿨롱효율과 비가역용량*

Qd = Qc x Eff (∴ Eff ; coulombic efficiency at the 1st cycle)

Qd = Qc-Qirr ⇒ Eff = f(Qc) ※ Function 도출 시험 필요

□ *전압변화*

V = f(Q,I)

Vb = f(Q,I) < 4.2V; Vc = f(q1,I) < 4.3V; Va = f(q3,I) > 0.0V

Vb = Vc - Va; Vbi = Vci - Vai; Vbf = Vcf - Vaf

∴ -i ; initial, -f ; final

□ *용량과 비용량*

유효비용량 = 유효용량/중량

Vc = f(정극유효비용량) ; Va = f(부극유효비용량)

∴ V ; also affected by the rate density

□ ***활물질 중량 및 용량비율 (Rw & Rc)***

Rw = m+/m- = 부극유효비용량/정극유효비용량

Rw_{max} = 부극비용량/정극비용량

$$Rc = \frac{Q_{da}}{Q_{dc}} = \frac{q_{da}}{q_{dc}R_w} = \frac{q_{ca}Eff_a}{q_{cc}Eff_cR_w}$$

□ ***활물질의 체적***

Vol(b) = Vol(c) + Vol(a) = Rw/dd(c)Ac(c) + 1/dd(a)Ac(a) (mL/g-carbon)

∴ dd ; apparent density, Ac ; content of active material

(b) ; battery, (a) ; anode, (c) ; cathode

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VI. 용량조화 해석

- ***용량조화 해석에 따른 Key Parameter로서 유효비용량 및 유효효율에 대한 반전지 시험결과 필요 즉, 충전비용량별 비용량, 비가역비용량, 효율 정보 필요***

① 전지/전극충전전위설정

전지충전전위설정 → 정극충전용량설정 - 부극충전용량설정
↓ ↓
정극충전전위설정 ↓
부극충전전위설정 → 부극충전 전위/용량 matching (Weight Control)
↓
Rw 도출

② 부극충전용량비율설정법

부극충전용량비율설정 → 부극충전비용량설정 → 부극충전종지전압설정
↓ ↓
정극충전비용량설정 ← 정극충전종지전위설정
↓
Rw 도출

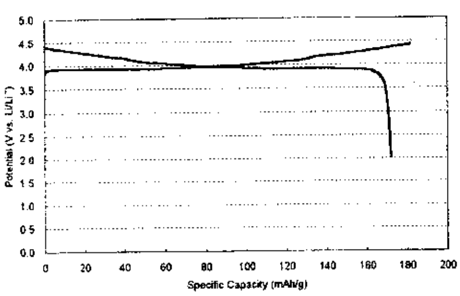
③ 정부극중량비설정법

Rw 설정 → 단위정극중량설정→ 정극전위용량관계계산
단위부극중량설정→ 부극전위용량관계계산
↓
전지충전전위설정 전지전위용량관계계산
↘ ↙
전지충전전위의 전지용량(≒정부극용량),
정부극비용량, 정부극전위 도출

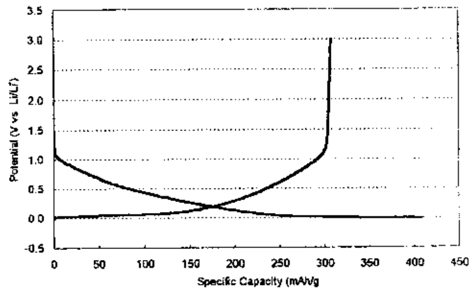
- ***본 용량설계에서 Parameter로 고려치 않은 사항***
  - Thermal Property
  - Temperature effect on cathode and anode specific capacity
  - Temperature effect on discharge capability
  - Rate capability
  - Capacity fading with cycling

VII. 전지용량설계에 필요한 전극재료 특성 도출

ㅁ 정·부극재료의 Potential Profiles

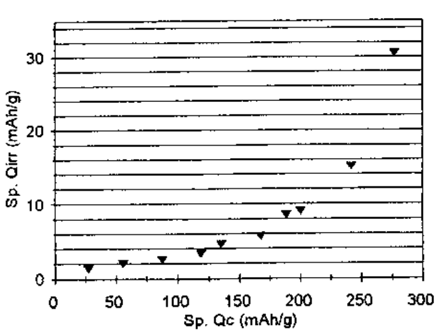


(a) $LiCoO_2$

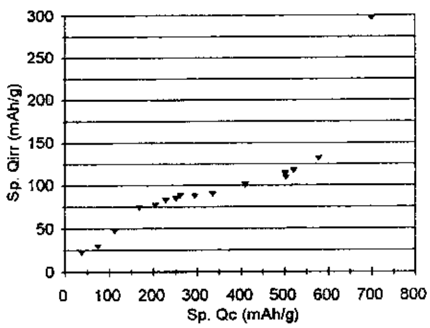


(b) hard carbon

ㅁ 정·부극재료의 충전비용량별 초기비가역비용량 특성



(a) $LiCoO_2$



(b) hard carbon

ㅁ Polynomial function of Q_{irr}

$LiCoO_2$; $Q_{irr} = -2.97+0.275Q_c-0.0055Q_c^2+5.1\times10^{-5}Q_c^3-2.08\times10^{-7}Q_c^4+3.19\times10^{-10}Q_c^5$

Hard Carbon ; $Q_{irr} = -79.68+2.18Q_c-0.0124Q_c^2+3.67\times10^{-5}Q_c^3-5.41\times10^{-8}Q_c^4+3.16\times10^{-11}Q_c^5$

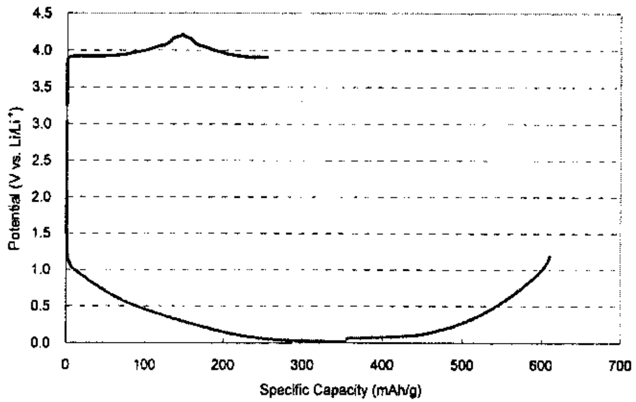
VIII. $LiCoO_2$/Hard Carbon ICR18650의 용량 설계

ㅁ 용량설계 원칙을 적용한 용량설계프로그램으로 전지용량 설계

■ Effective Specific Capacity vs. Potential Diagram

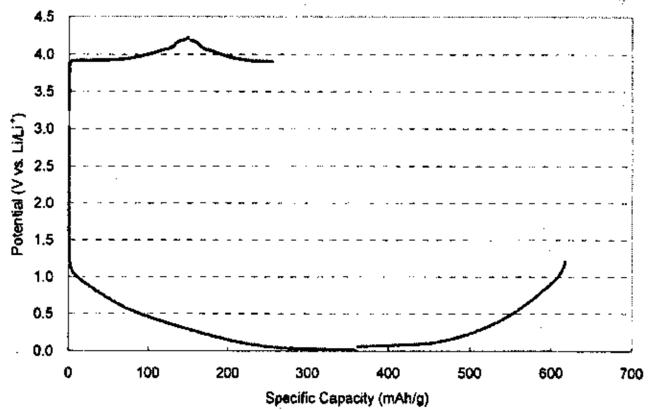
By Voltage Regulation

; 4.2V Battery Voltage



By Rw Regulation

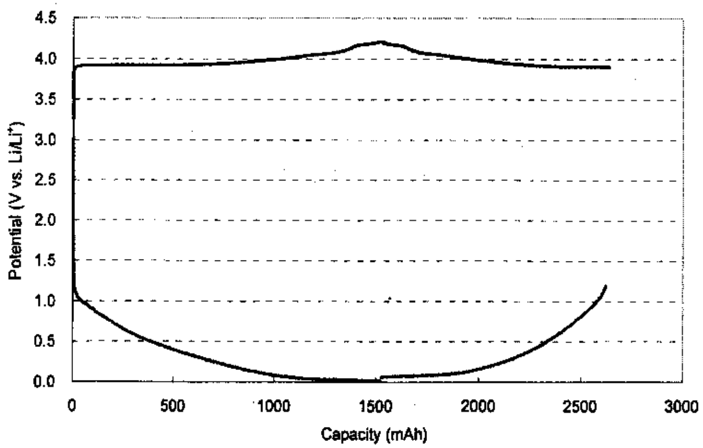
; Rw = 2.4



■ **ICR18650 Battery Capacity vs. Potential Diagram**

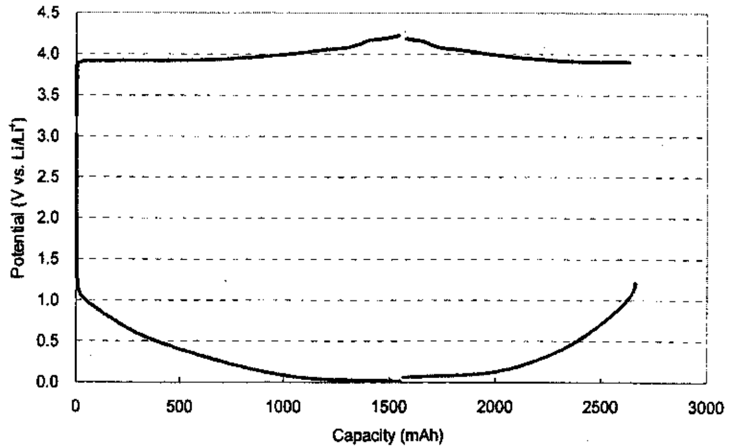
By Voltage Regulation

; 4.2V Battery Voltage



By Rw Regulation

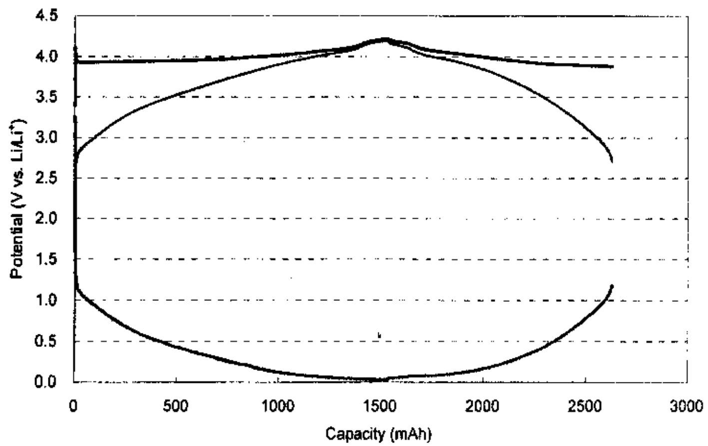
; Rw = 2.4



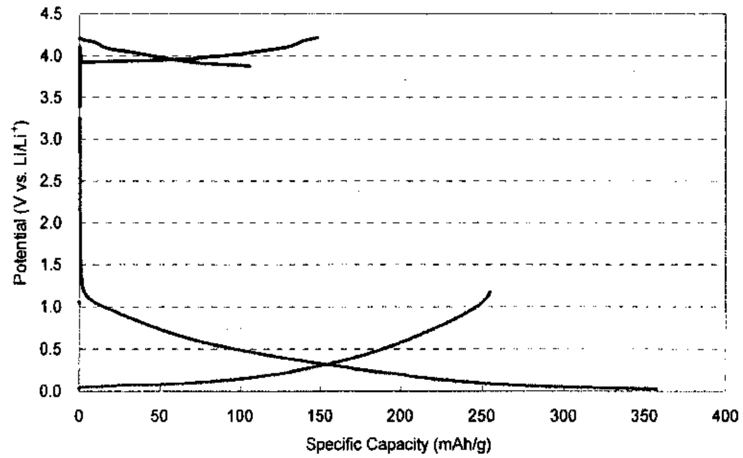
IX. $LiCoO_2$/Hard Carbon ICR18650의 용량 시험

Battery Charge Limit Voltage ; 4.2V, Rw ; 2.414

Battery Capacity vs. Potential



Effective Specific Capacity vs. Potential



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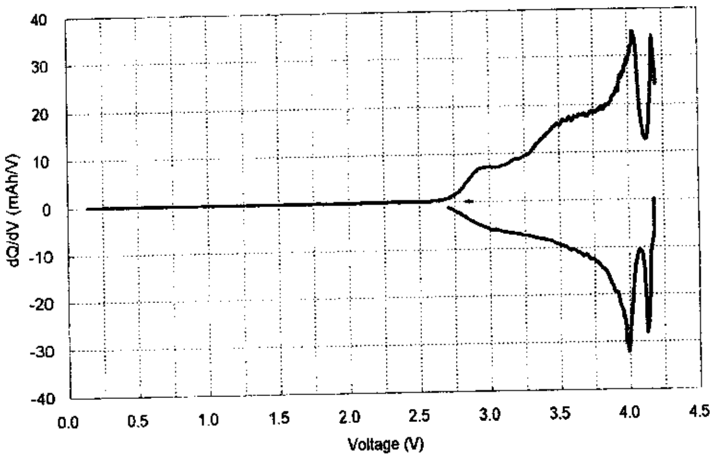
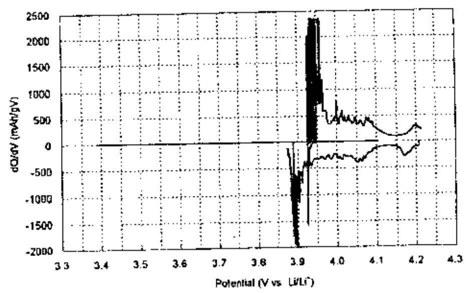
■ Differential Chronopotentiogram

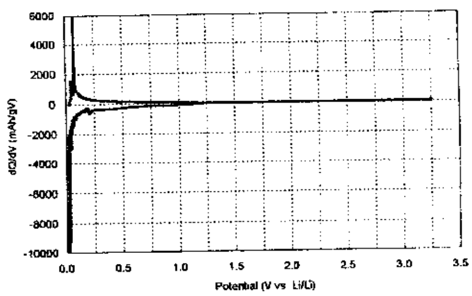
Based on Battery Voltage



Based on Cathode Potential



Based on Anode Potential



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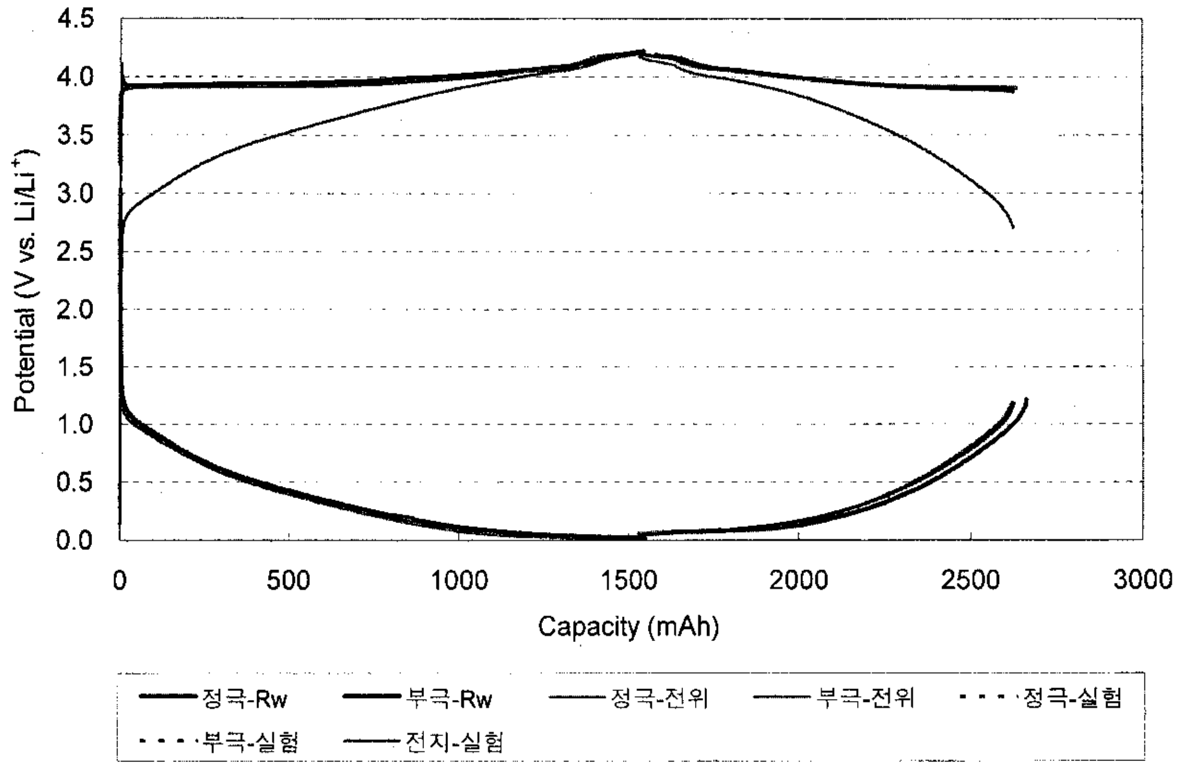
X. 용량 설계 및 시험 결과 비교



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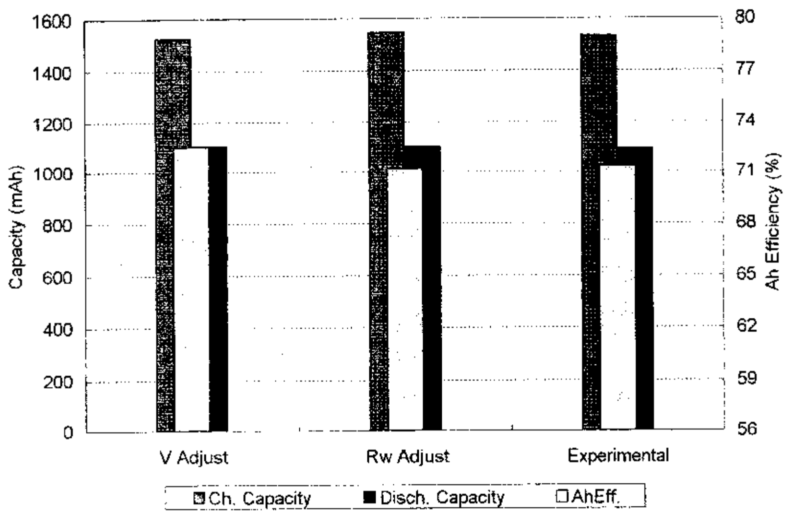

XI. 결론

- 리튬이온전지의 용량설계법 개발
- 정극 및 부극 재료의 충전용량별 충방전 특성 도출
- Material Balance 수행
- $LiCoO_2$/hard carbon ICR18650의 전지용량계산
- Test cell 평가에 의한 계산결과의 검증