다공성 고분자가 코팅된 겔화 세퍼레이터를 이용한 리튬이온폴리머전지

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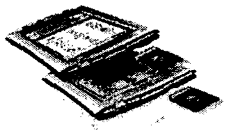
한밭대학교

Li-Ion Polymer Batteries Constructed with Porous Polymer-Coated Gelling Separators



2003. 11. 21

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이차전지의 요구특성

✓ High Energy Density

✓ Concern on Electrolyte Leakage

✓ Improved Safety

✓ High Rate Capability (Low Impedance)

✓ Wide Operating Temperature Range (-20 ~ 60 °C)

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리튬이차전지

	리튬이온전지 (Lithium Ion Battery)	리튬이온폴리머전지 (Lithium Ion Polymer Battery)	리튬금속폴리머전지 (Lithium Metal Polymer Battery)
음 극	탄소	탄소	리튬
전해질	액체전해질	고분자전해질	고분자전해질
양 극	금속산화물 ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ 등)	금속산화물 ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ 등)	금속산화물,유기설퍼,전도성고분자
평균전압	3.6 V	3.6 V	2.0 - 3.6 V
에너지밀도	high	high	very high
싸이클특성	excellent	good	poor
저온 특성	good	medium	poor
안 전 성	poor	medium	good
셀디자인의 자유도	poor	good	good

유기전해질의 분류

1. 액체 전해액

① 비친용매 격리막형 : 폴리올레핀 세퍼레이터 + 전해액

② 친용매 격리막형 : PVdF 다공성 세퍼레이터 + 전해액

2. 겔 고분자 전해질

① 선형 고분자형(물리적 가교형) : PEO,PAN,PMMA,PVdF + 전해액

② 가교 고분자형(화학적 가교형) : 올리고머(단량체) + 가교제 + 전해액

3. 고체 고분자 전해질

고분자(PEO 계) + 염 + (무기필러)

고분자 전해질의 요구특성

☺ 이온전도도

- 10^{-3} S/cm 이상이면 실용화 가능

☹ 기계적 특성

- 박막을 제조하기 위한 우수한 기계적 강도가 요구됨
- 제품의 scale-up 시 중요한 고려사항임

☺ 전기화학적 안정성

- 전극물질에 inert 해야 함
- 작동전압 내에서 안정해야 함

☺ 전해액과의 상용성

- 유기용매가 고분자내에 효과적으로 encapsualation 되어야 함(누액방지)

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겔 고분자 전해질의 제조

1. Solution casting 법
   - 고분자/전해액/(무기필러)을 공통용매에 용해시킨 후, casting하여 공용매를 제거한 후 필름을 얻음
   - 장점 : 쉽고 경제적임(기존설비 활용가능)
   - 단점 : 전해액의 조성 유지가 어려움

   예) PEO계, PMMA계

2. Hot melting법
   - 고온(~ 120 ℃)에서 고분자를 전해액에 직접 용해시킨 후, 상온으로 냉각시켜 겔화된 필름을 얻음
   - 장점 : 공용매를 사용할 필요가 없으며, 전해액의 조성 유지 가능
   - 단점 : 비점이 낮은 전해액은 사용할 수 없음

   예) PAN계

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3. In-situ crosslinking 법

- 반응성 올리고머, 가교제, 전해액을 섞어 열 또는 UV 조사를 통해 3차원 network 구조를 갖는 겔 고분자 전해질을 얻음
- 장점 : 필름의 기계적 물성이 우수함
- 단점 : 가교공정이 포함되어 생산성이 떨어짐, 미 반응물이 잔존함

예) PEGDMA계

4. 다공성막 침적법

- 전해액과 친화성이 있는 고분자를 사용하여 다공성 막을 제조한 후, 이를 전해액에 침적시켜 겔화시킴
- 장점 : 무수분위기 요구 시간이 짧음, 다양한 전해액을 적용할 수 있음
- 단점 : 전해액의 균일한 분산이 어려움(aging 필요)

예) P(VdF-co-HFP)계

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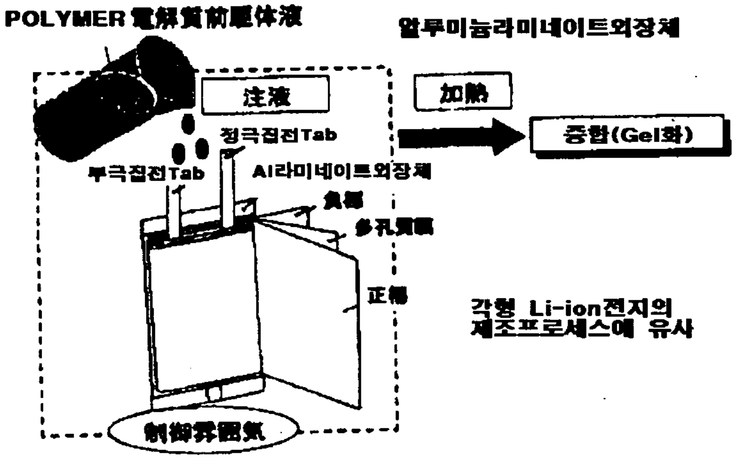
LIPB by SANYO



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Features of SANYO Polymer Battery

1. Cross-linked structure of polymer electrolyte
   - fast holding of liquid electrolyte ⇒ high performance
   - complete gel ⇒ high reliability

2. Polymerization in battery case
   - good interface between electrode and electrolyte
   - utilization of LIB manufacturing technology ⇒ high productivity

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Research Background

기계적 강도가 높은 겔화 가능한 박막의 다공성 막을 제조하여,

이들로부터 리튬이차전지에 적용 가능한 겔 고분자 전해질을 개발함

1) 이온전도 특성이 우수하고,

2) 기계적 특성이 우수하여 핸들링(scale-up 공정)이 가능하며,

3) 전해액 누액현상이 없으며,

4) 전기화학적으로 안정한 특성

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Preparation of Gel Polymer Electrolytes

Study 1	Study 2
Preparation of Porous Membrane	Coating of Gelable Polymer on Separator
↓	
Soaking of Membrane in Electrolyte Solution	Soaking of Separator in Electrolyte Solution
↓	
Gelation of Membrane	Gelation of Polymer on Separator

Study 1   *Study 2*

Study 1: Gel Polymer Electrolytes Based on Porous PAN Membranes for Rechargeable Lithium-Ion Polymer Batteries

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Electrolyte Uptake

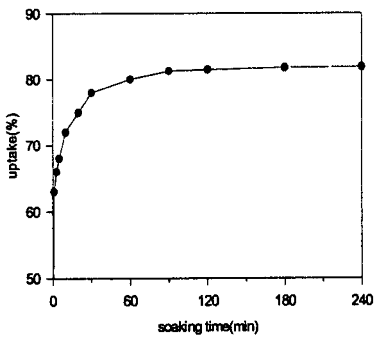

Fig. Uptake of electrolyte solution as a function of soaking time(1.0 M $LiPF_6$- EC/DMC).

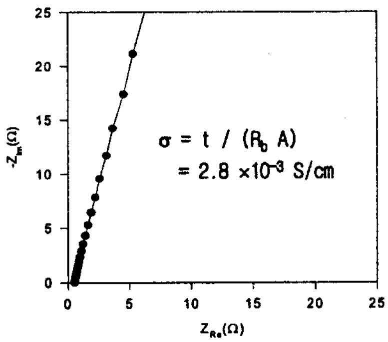

Fig. AC impedance spectrum of the SS/PAN /SS cell.

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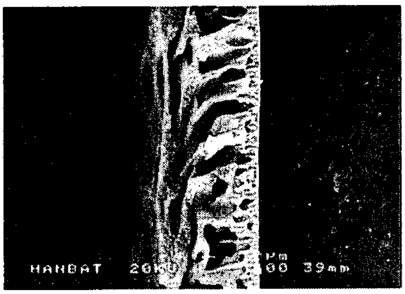
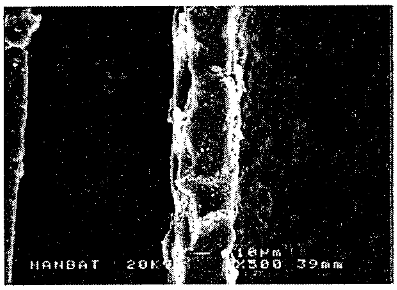
Microstructure of Gelled Membrane



(a) before soaking in electrolyte



(b) after soaking in electrolyte

Fig. SEM images of the cross section of porous PAN membrane and gelled PAN membrane.

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Ionic Conductivity

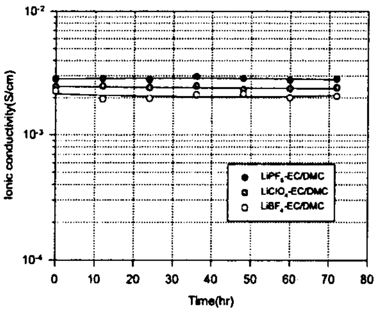

Fig. Time evolution of ionic conductivity of the porous PAN membrane soaked with different electrolyte solution.

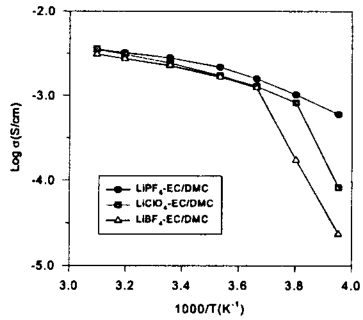

Fig. Temperature dependence of ionic conductivity for PAN membrane prepared with different electrolyte solution.

Electrochemical Stability

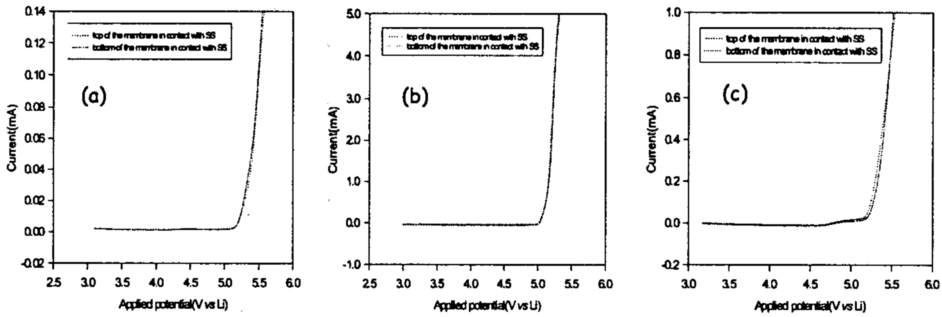

Fig. Linear sweep of the cell prepared with a porous PAN membrane containing (a) $LiPF_6$-EC/DMC, (b) $LiClO_4$-EC/DMC, (c) $LiBF_4$-EC/DMC (scan rate = 1 mV/s).

Cycling Performances

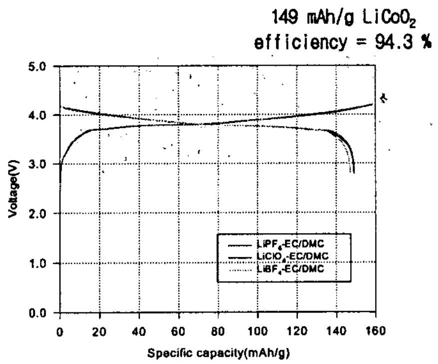

Fig. First preconditioning cycles of lithium-ion polymer cells prepared with porous PAN membranes.

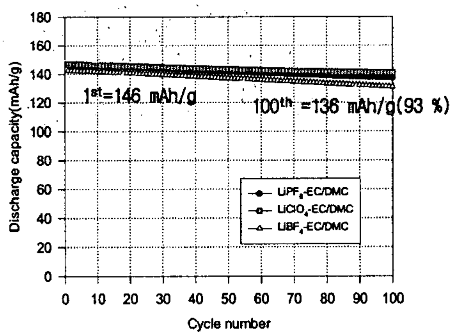

Fig. Discharge capacity of lithium-ion polymer cell as a function of cycle number.

Rate Capability

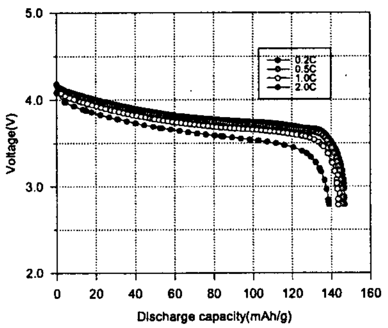

Fig. Discharge profiles of a lithium-ion polymer cell prepared with $LiPF_6$-EC/DMC.

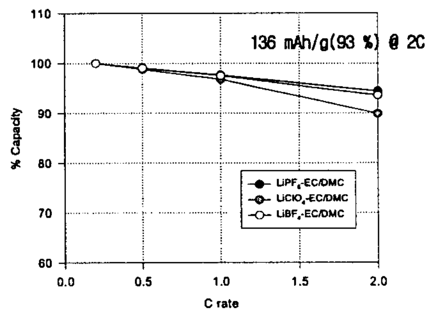

Fig. Discharge capacities of a lithium-ion polymer cells as a function of C rate.

Study 2. Porous Polymer-Coated Gelling Separator for Lithium-Ion Polymer Batteries

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Microstructure

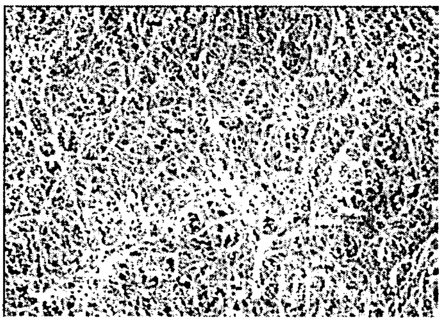

Fig. SEM image of a PE separator.

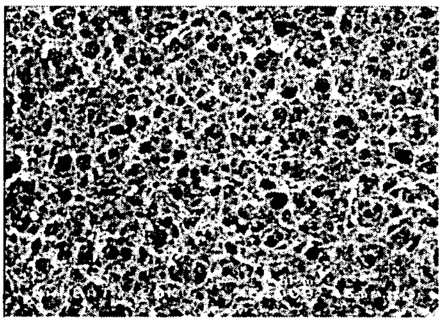

Fig. SEM image of a polymer-coated separator. (coated with 3 % solution)

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Electrochemical Stability

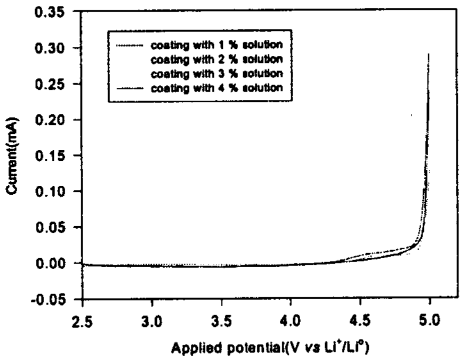

Fig. Linear sweep voltammetry curves of the cells prepared with the polymer-coated separators soaked by $LiClO_4$-EC/DMC(SR = 1 mV/s).

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1st Ch/Discharge Cycle

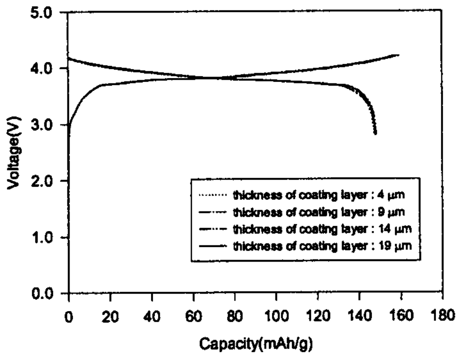

Fig. First preconditioning cycles of the lithium-ion polymer cells prepared with polymer-coated separators(C/10 rate)

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AC Impedance (1)

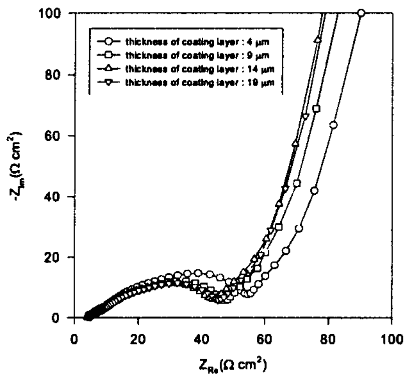

Fig. *AC impedance spectra of the lithium-ion polymer cells prepared with the polymer -coated separators of different coating layer thickness, which are measured after the preconditioning cycle.*

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Table. Electrolyte resistance(R_e) and interfacial resistance(R_i)

Thickness of coating layer (μm)	R_e(Ω cm²)	R_i(Ω cm²)	R_t(Ω cm²)[a]
4	4.3	50.4	54.7
9	4.2	43.2	47.4
14	4.0	40.1	44.1
19	4.9	40.4	45.3

[a] : The value of R_t means total resistance of the cell(R_e + R_i).

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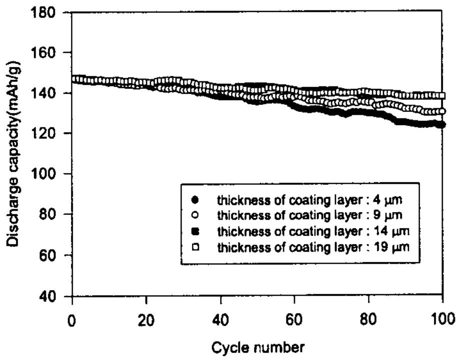
Cycle Life (1)



1^{st} = 147.2 mAh/g
100^{th} = 137.4 mAh/g(93.3 %)

Fig. Discharge capacities of lithium-ion polymer cells as a function of cycle number.

AC Impedance (2)

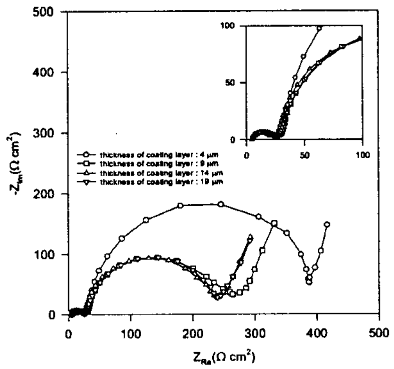


Fig. A.C. impedance spectra lithium-ion polymer cells at fully discharged state after 100 charge/discharge cycles

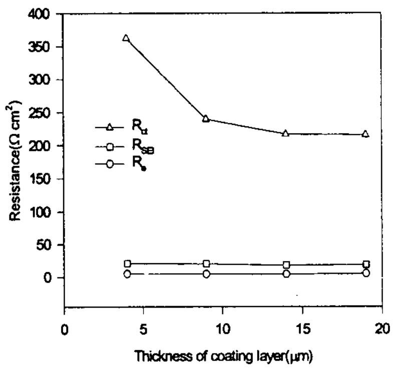


Fig. Variation of R_e, R_{SEI} and R_{ct} with thickness of gel layer in the cells after the repeated 100 cycles.

Rate Capability

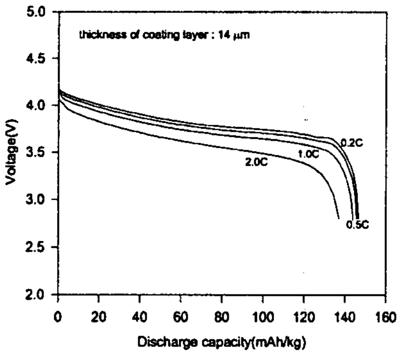


Fig. Discharge profiles of a lithium-ion polymer cell as a function of C rate.

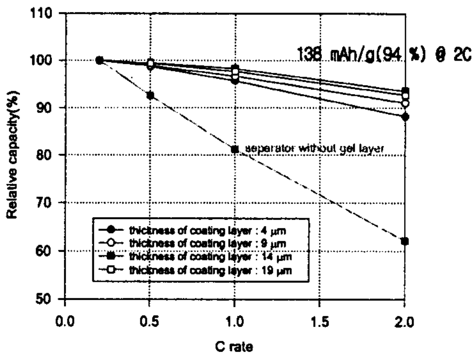


Fig. Discharge capacities of lithium-ion polymer cells as a function of C rate.

Cycle Life (2)

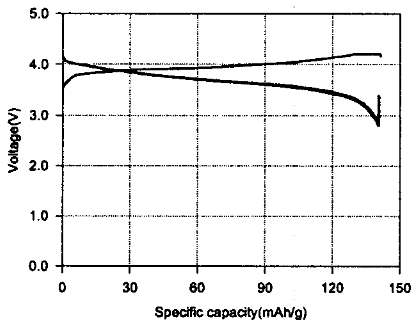


Fig. Charge and discharge curves of the lithium-ion polymer cell (charge : 0.5 CC & CV, discharge : 0.5 CC, from 21st to 25th cycles)

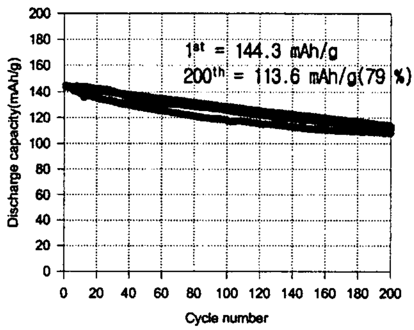


Fig. Discharge capacities of lithium-ion polymer cells as a function cycle number (charge : 0.5 CC & CV, discharge : 0.5 CC).

Li/$LiCoO_2$ Cells

cycling characteristics

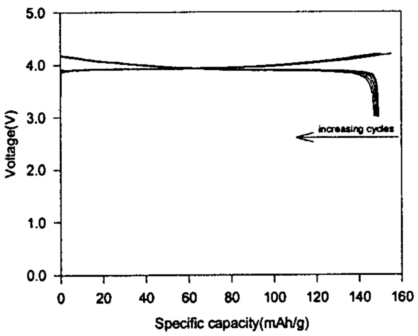


Fig. Charge and discharge curves of the Li/$LiCoO_2$ cell at 0.24 mA/cm^2.(1,2,3,4,5th cycle)

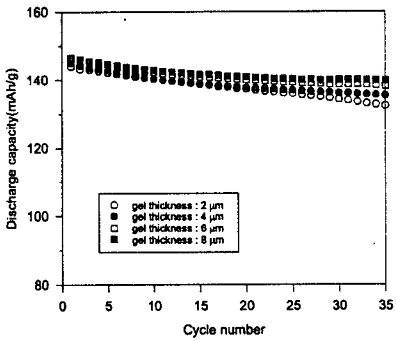


Fig. Discharge capacities as a function cycle number for the Li/$LiCoO_2$ cells prepared with the separator of different gel thickness.

Li/$LiCoO_2$ Cells

rate capability

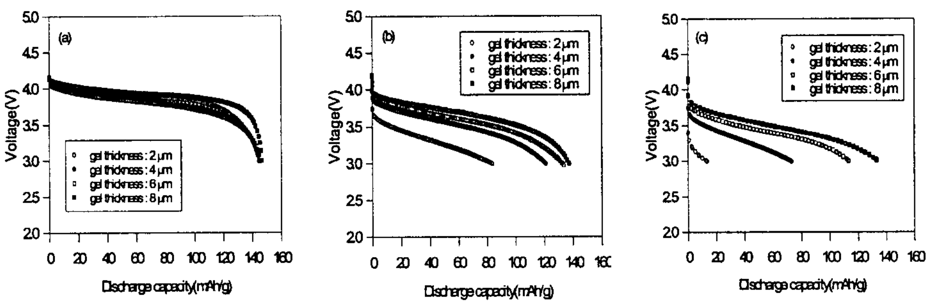


Fig. Discharge profiles of the Li/$LiCoO_2$ cells prepared with the separator of different gel thickness, which are obtained at different current rate. (a) 0.48 mA/cm^2, (b) 1.20 mA/cm^2, (c) 2.40 mA/cm^2

Li/$LiCoO_2$ Cells

AC impedance analysis

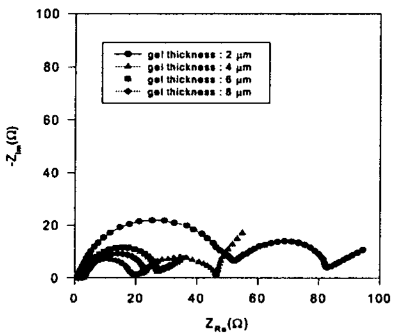


Fig. *AC impedance spectra of Li/$LiCoO_2$ cells, which are measured after the repeated 35 cycles*

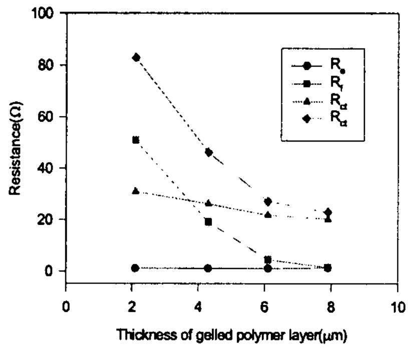


Fig. *Variation of R_e, R_f and R_{ct} in the Li/$LiCoO_2$ cells with thickness of gel layer after the repeated 35 cycles*

Conclusions

1) The porous polymer coated on both sides of PE separator was gelled in contact with the electrolyte solution and encapsulated a larger amount of electrolyte solution.

2) Gel layer on both sides of PE separator promoted strong interfacial adhesion between electrodes and separator, and the intimate contact was proven to be essential for good capacity retention in the cell.

3) Cycling performances of the cells were shown to be dependent on the thickness of gel layer on PE separator.

4) The lithium-ion (lithium metal) polymer cells prepared with the polymer-coated separator exhibited a stable discharge capacity and good rate performance even though packed in a flexible plastic pouch.

☞ Polymer-coated separator with proper thickness of gel layer is a promising electrolyte material for rechargeable lithium batteries.

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