
리튬 이차전지용 Cathode 재료의 전기화학

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cathode 재료의 전기화학**

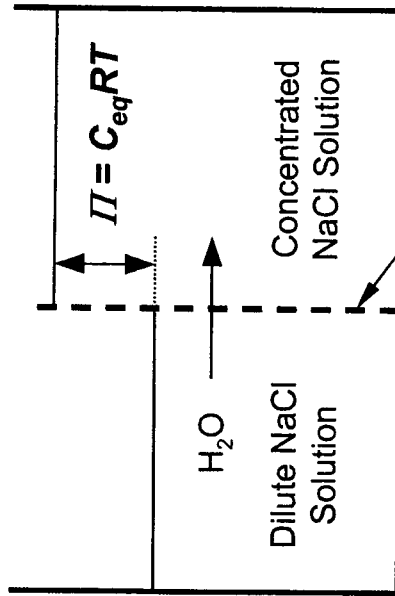
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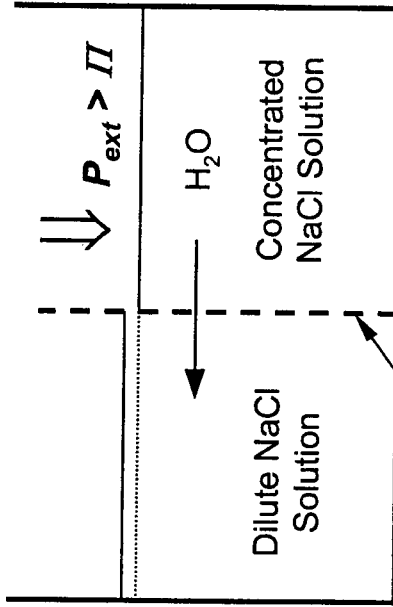
Galvanic cell vs. Electrolysis cell

Osmosis



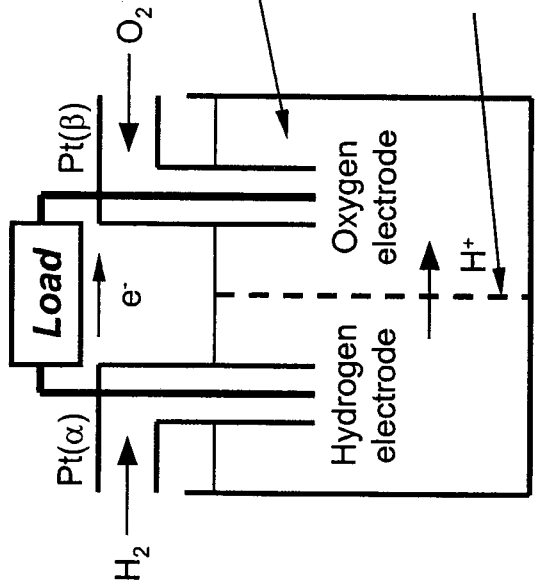
Flexible, semipermeable membrane

Reverse osmosis of sea water

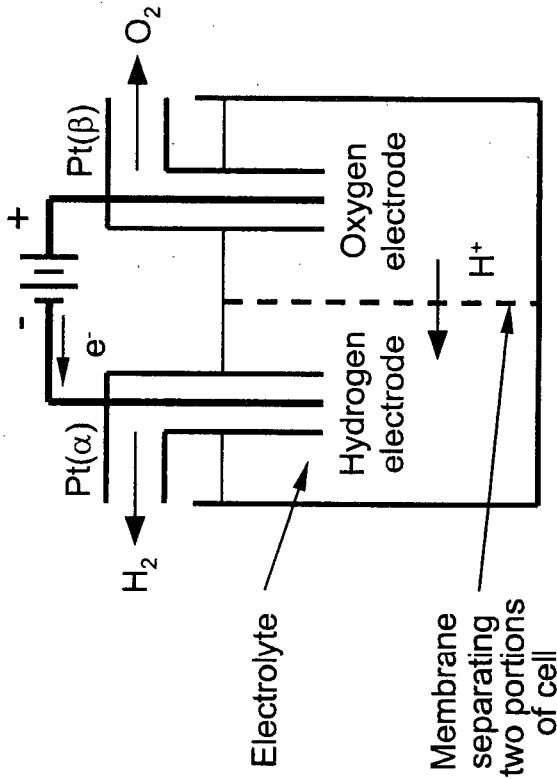


At equilibrium between dilute and concentrated NaCl solutions

H₂ - O₂ fuel cell



Electrolysis of H₂O



Chemical equilibrium :

$$H_2 + 1/2 O_2 = H_2O$$

Electrochemical equilibrium :

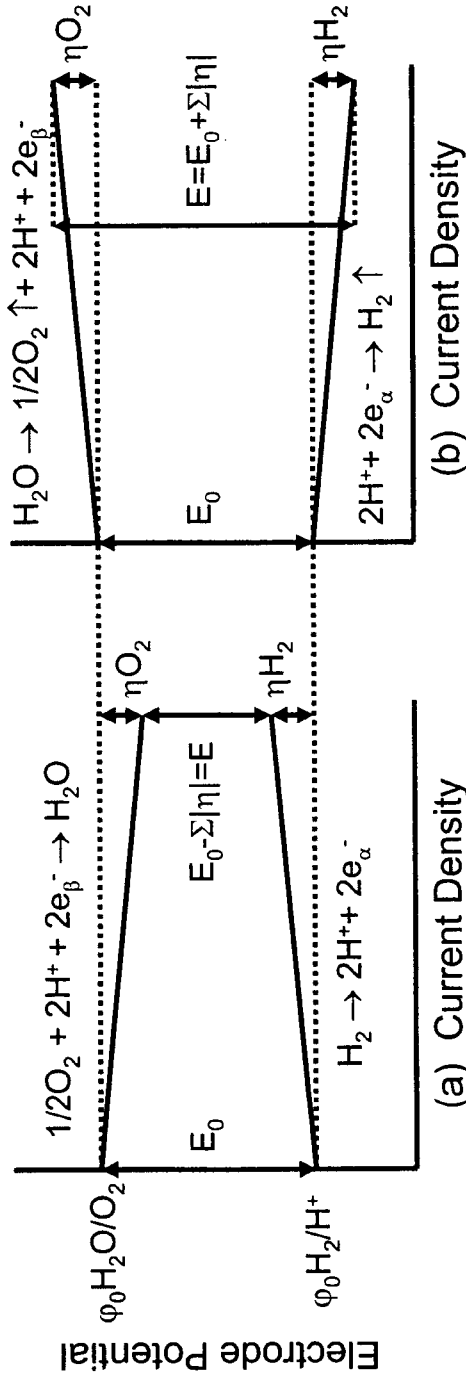
$$H_2 = 2H^+ + 2e_\alpha$$

$$+) \quad 1/2 O_2 + 2H^+ + 2e_\beta = H_2O$$

$$\Rightarrow H_2 + 1/2 O_2 + 2e_\beta = H_2O + 2e_\alpha$$

Galvanic cell vs. Electrolysis cell

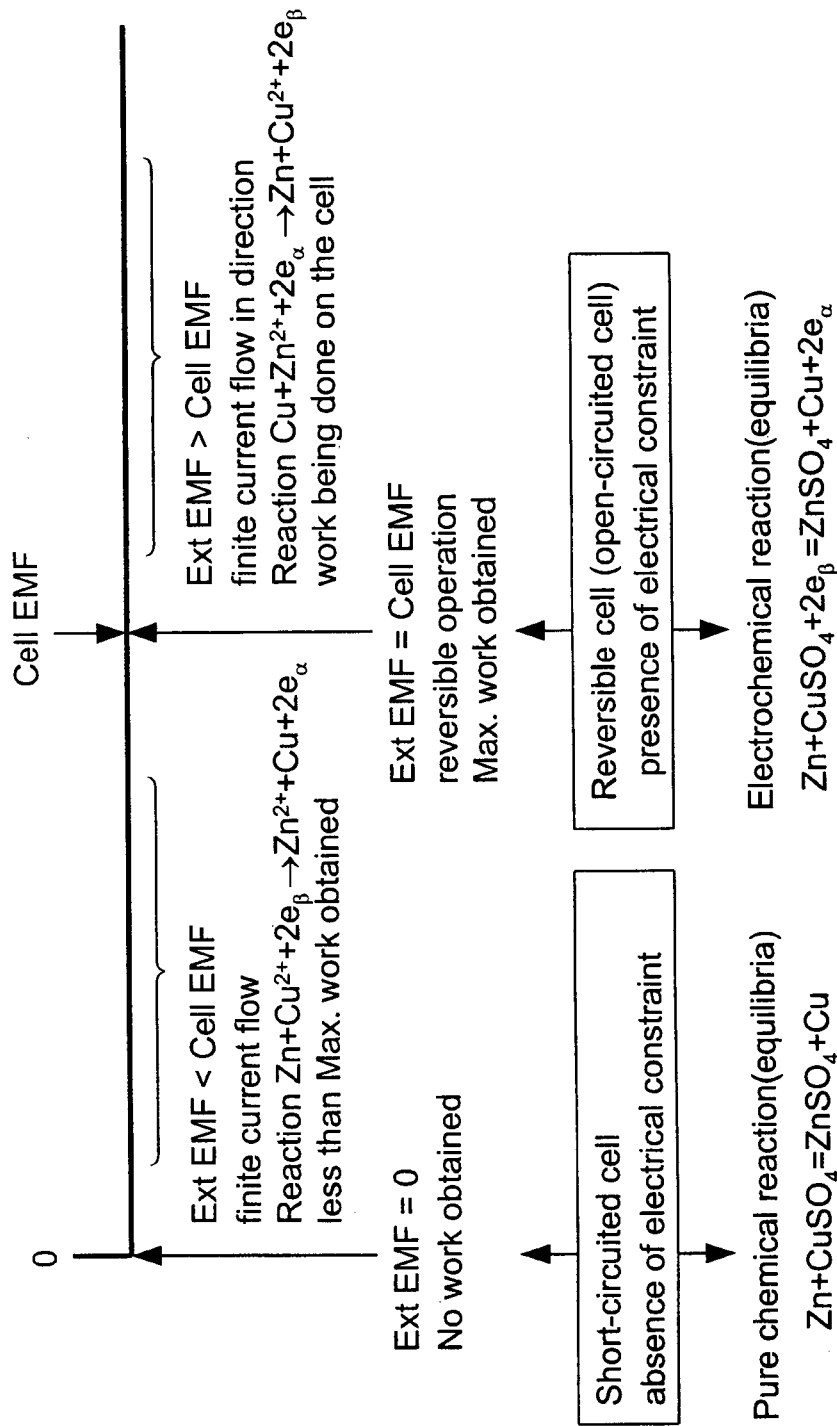
- **Galvanic cell** : self-driven cell
 \Rightarrow chemical energy \rightarrow electrical energy
- **Electrolysis cell** : externally-driven cell
 \Rightarrow electrical energy \rightarrow chemical energy



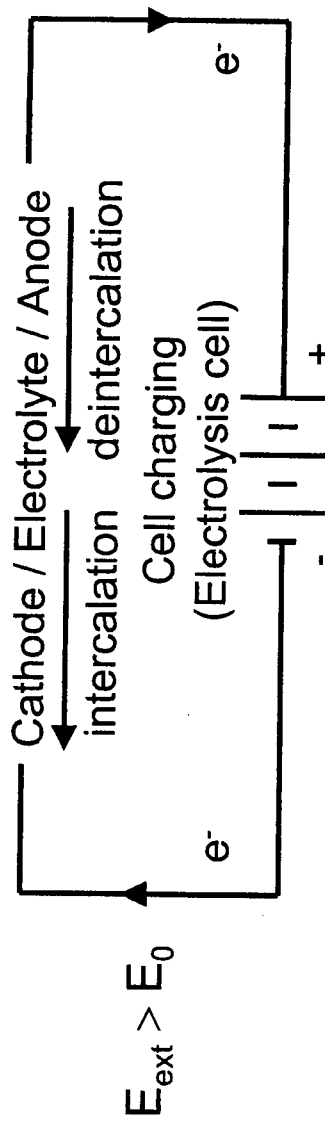
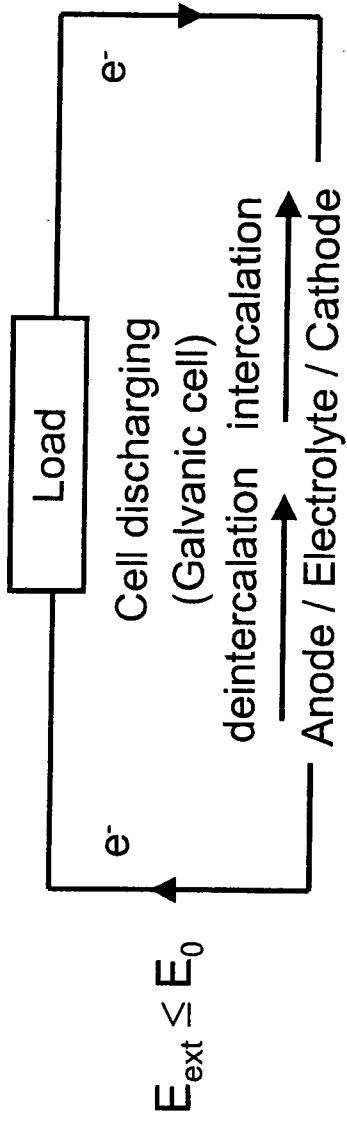
$\Rightarrow E_{\text{discharge}} < E_0 < E_{\text{charge}}$ at any time

Schematic diagram of polarization curves for (a) H₂-O₂ fuel cell and (b) electrolysis of H₂O

Relationship of a galvanic cell to a electrolysis cell

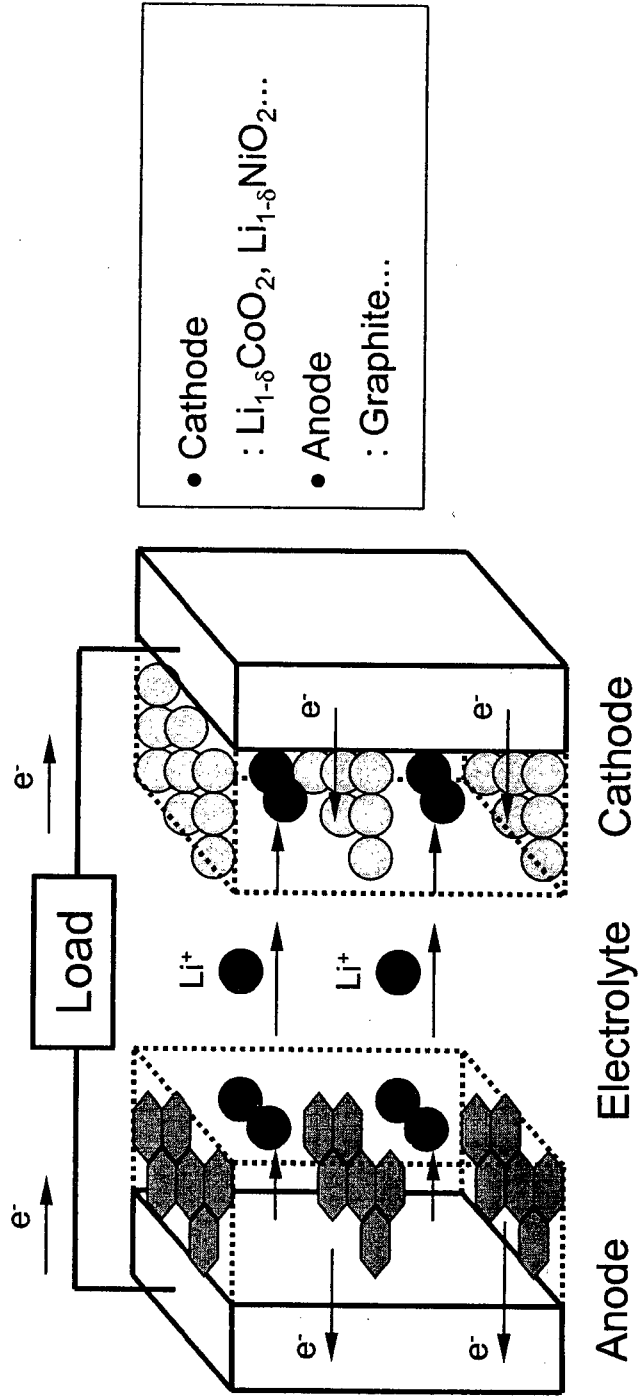
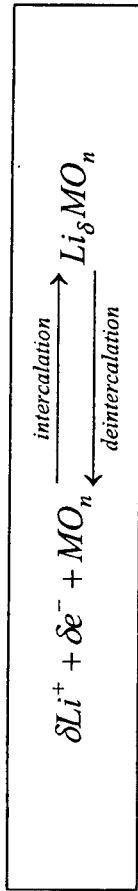


Terminology used for MH & Li Ion Batteries



- Intercalation = Insertion = Injection
- Deintercalation = Desertion = Extraction

Discharging of Li Ion Battery

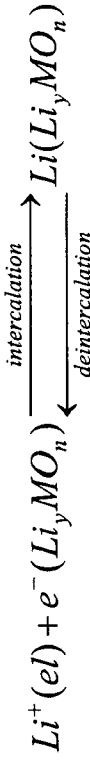


Cell Voltage of Li Ion Battery

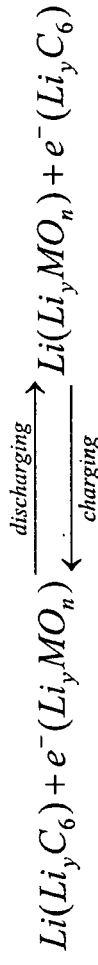
Electrochemical lithium intercalation into carbon (anode)



Electrochemical lithium intercalation into transition metal oxide (cathode)



Overall reaction of cell



Nernst equation $\sum v_i \eta_i = \sum v_i (\mu_i + z_i F \phi) = 0$

Galvani potential difference between anode and cathode

$$\phi(\text{Li}_y\text{MO}_n) - \phi(\text{Li}_y\text{C}_6) = \frac{\mu_{\text{Li}^+ (\text{Li}_y\text{C}_6)}^0 - \mu_{\text{Li}^+ (\text{Li}_y\text{MO}_n)}^0}{F} + \frac{RT}{F} \left[\ln a_{\text{Li}^+ (\text{Li}_y\text{C}_6)} - \ln a_{\text{Li}^+ (\text{Li}_y\text{MO}_n)} \right] \quad (1)$$

Cell Voltage of Li Ion Battery

Open circuit voltage

$$\Delta V_{\text{cell}} = \frac{\eta_{e^-(\text{Cu})} - \eta_{e^-(\text{Cu}')}}{F} = \frac{\mu_{e^-(\text{Cu})} - \mu_{e^-(\text{Cu}')}}{F} - [\varphi(\text{Cu}) - \varphi(\text{Cu}')] = \varphi(\text{Cu}') - \varphi(\text{Cu})$$

$$\eta_{e^-(\text{Cu})} = \eta_{e^-(\text{Li}_y\text{C}_6)}; \quad \mu_{e^-(\text{Cu})} - F\varphi(\text{Cu}) = \mu_{e^-(\text{Li}_y\text{C}_6)} - F\varphi(\text{Li}_y\text{C}_6)$$

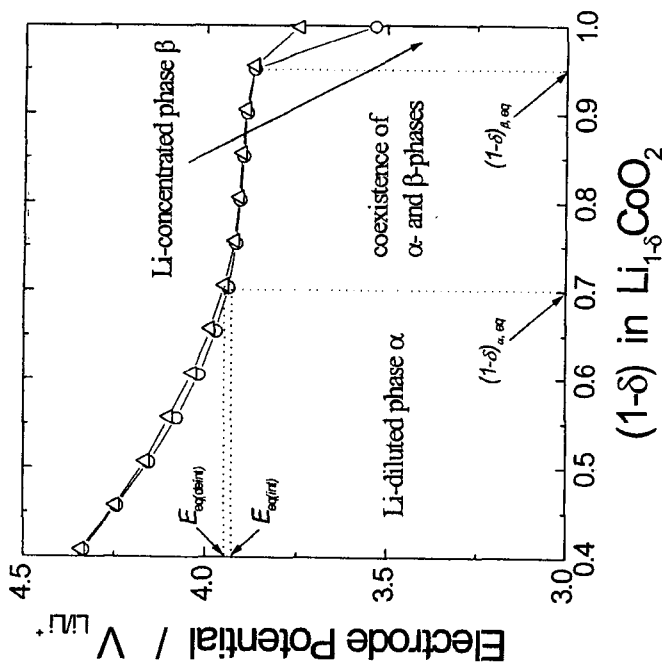
$$\eta_{e^-(\text{Cu}')} = \eta_{e^-(\text{Li}_y\text{MO}_n)}; \quad \mu_{e^-(\text{Cu}')} - F\varphi(\text{Cu}') = \mu_{e^-(\text{Li}_y\text{MO}_n)} - F\varphi(\text{Li}_y\text{MO}_n)$$

$$\Delta V_{\text{cell}} = \frac{\eta_{e^-(\text{Cu})} - \eta_{e^-(\text{Cu}')}}{F} = \varphi(\text{Cu}') - \varphi(\text{Cu}) = \underbrace{\varphi(\text{Li}_y\text{MO}_n) - \varphi(\text{Li}_y\text{C}_6)}_{(1)} + \frac{\mu_{e^-(\text{Li}_y\text{C}_6)} - \mu_{e^-(\text{Li}_y\text{MO}_n)}}{F}$$

$$\begin{aligned} \Delta V_{\text{cell}} &= \frac{\mu_{\text{Li}^+(\text{Li}_y\text{C}_6)}^0 - \mu_{\text{Li}^+(\text{Li}_y\text{MO}_n)}^0}{F} + \frac{RT}{F} \left[\ln a_{\text{Li}^+(\text{Li}_y\text{C}_6)} - \ln a_{\text{Li}^+(\text{Li}_y\text{MO}_n)} \right] \Rightarrow \Delta V_{\text{lithium ion}} \\ &+ \frac{\mu_{e^-(\text{Li}_y\text{C}_6)}^0 - \mu_{e^-(\text{Li}_y\text{MO}_n)}^0}{F} + \frac{RT}{F} \left[\ln a_{e^-(\text{Li}_y\text{C}_6)} - \ln a_{e^-(\text{Li}_y\text{MO}_n)} \right] \Rightarrow \Delta V_{\text{electron}} \end{aligned}$$

Open circuit voltage of cell is related to the activity of lithium ion in transition metal oxide cathode and carbon anode and the chemical potential of electron in both electrodes

Galvanostatic Charge-discharge Curve obtained from Porous $\text{Li}_{1-\delta}\text{CoO}_2$ Electrode



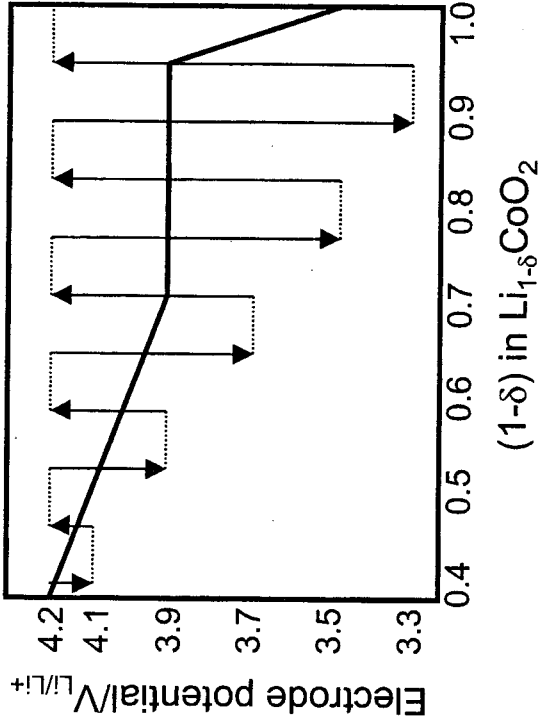
Wide potential plateaux near $3.90 V_{\text{Li/Li}^+}$ in the $(1-\delta)$ range 0.7 to 0.95
 \Rightarrow the coexistence of two phases of a Li-diluted phase α and a Li-concentrated phase β

Electrode potential obtained from porous $\text{Li}_{1-\delta}\text{CoO}_2$ electrode in 1 M LiClO_4 -PC solution as a function of lithium content $(1-\delta)$ during lithium intercalation(o) and deintercalation (Δ). The change of lithium content of $\Delta\delta = 1$ for $\text{Li}_{1-\delta}\text{CoO}_2$ occurs over 5 h.

Potentiostatic Current Transient Technique

1. Large potential step condition

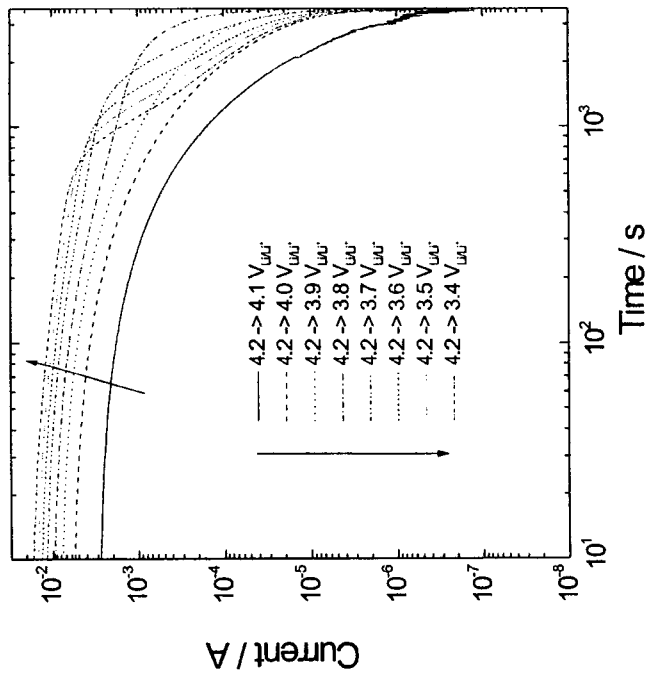
- initial potential (E_1) : $4.2 V_{\text{Li/Li}^+}$
- lithium injection potential (E_2) : $3.3, 3.5, 3.7, 3.9, 4.1 V_{\text{Li/Li}^+}$
- Equilibrium potential for the lithium intercalation ($E_{\text{eq, inter}} = 3.90 V_{\text{Li/Li}^+}$)
- driving force for phase boundary movement for the lithium intercalation = $(E_{\text{eq, inter}} - E_2)$



concentration gradient > electrical potential (galvani potential) gradient

- * The lithium transport through the oxide electrode in the single phase region runs by simple finite-length diffusion within a single phase α
- * The lithium transport through the oxide electrode in the two-phase coexistence region may proceed by the phase boundary movement

Potentiostatic Current Build-up Transient



Above 3.90 V_{Li/Li+}
two-stage current transient
 => simple finite-length diffusion of lithium ions through the single α phase

Below 3.90 V_{Li/Li+}
three-stage current transient
 => phase boundary movement
 (phase transformation from α to β)

Potentiostatic build-up current transient on a logarithmic scale obtained from porous Li_{1- δ} CoO₂ electrode in 1 M LiClO₄-PC solution.

Theory of Two-stage Current Transient

* Potentiostatic lithium injection into the electrode subjected to an impermeable constraint

$$I(t) = \frac{Q\sqrt{\bar{D}_{Li^+}}}{L\sqrt{\pi}}$$

$$t \ll \frac{L^2}{\bar{D}_{Li^+}}$$

$I(t)$; cathodic current

t ; lithium injection time

$$I(t) = \frac{2Q\bar{D}_{Li^+}}{L^2} \exp\left(-\frac{\pi^2 \bar{D}_{Li^+}}{4L^2} t\right)$$

$$t \ll \frac{L^2}{\bar{D}_{Li^+}}$$

Q ; total charge transferred during lithium intercalation

\bar{D}_{Li^+} ; the chemical diffusivity of lithium ion

L ; the thickness of the electrode with planar symmetry

Since *the change in shape of the transient* is of greater significance than the absolute current level, it is very effective to introduce *the derivative of logarithmic current with respect to logarithmic time*

$$\frac{\partial \log I(t)}{\partial \log t} = -\frac{1}{2}$$

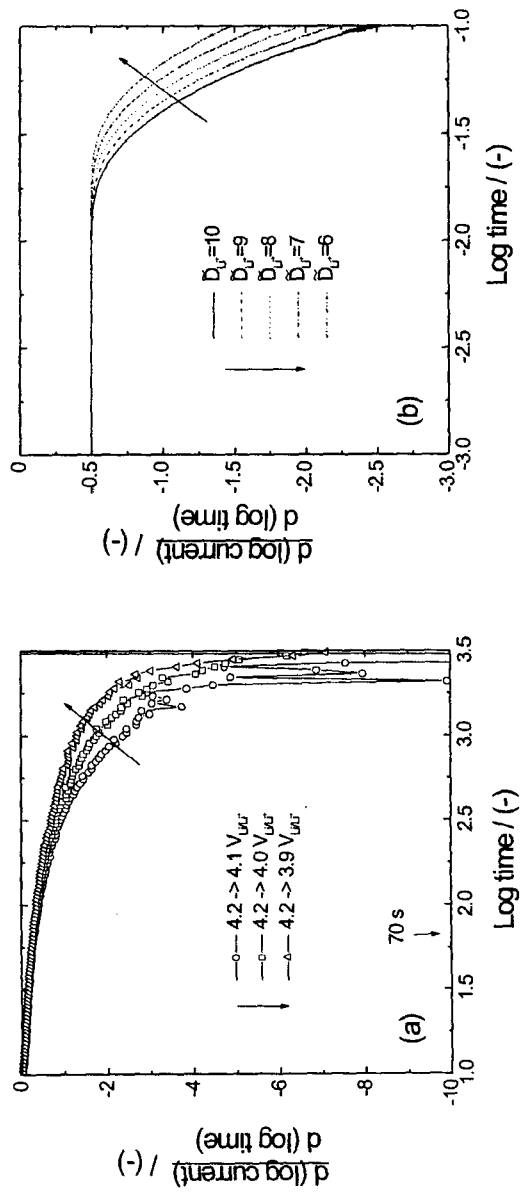
$$t \ll \frac{L^2}{\bar{D}_{Li^+}}$$

The derivative shows a constant value in the initial stage and an exponential growth in the negative direction in the later stage

$$\frac{\partial \log I(t)}{\partial \log t} = -\frac{\pi^2 \bar{D}_{Li^+} \log e}{4L^2} \exp(2.3 \log t), \quad t \ll \frac{L^2}{\bar{D}_{Li^+}}$$

Derivative of Two-stage Current Transient

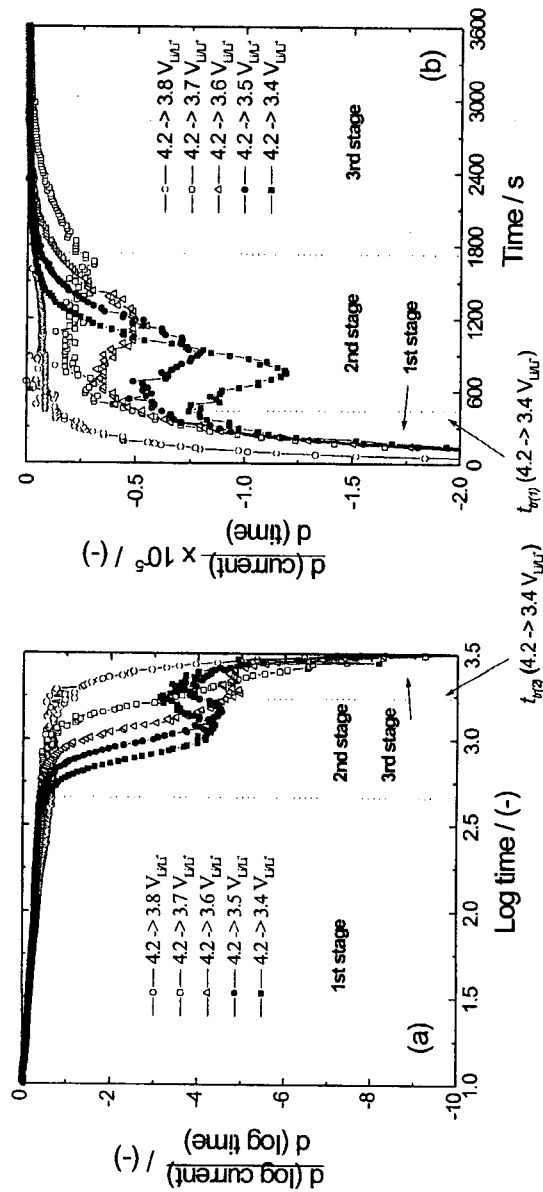
Chemical diffusivity of lithium ion decreases with lowering lithium injection potential, i.e. with increasing equilibrium lithium content



The derivatives of the logarithmic build-up current transients (a) experimentally determined at various lithium injection potentials above the quasi-equilibrium potential and (b) obtained from numerical solution to the Fick's diffusion equations at various chemical diffusivities for the potentiostatic lithium injection into the electrode subjected to the impermeable constraint.

Derivative of Three-stage Current Transient

The values of the first transition time $t_{tr(1)}$ and the second transition time $t_{tr(2)}$ could be taken from the derivatives of the linear and the logarithmic current transients, respectively.



The derivatives of the (a) logarithmic and (b) linear current transients experimentally obtained at various lithium injection potentials below the quasi-equilibrium potential.

Theory of Three-stage Current Transient

* Moving Phase Boundary Problem

- change of concentration gradients across the phase β

$$\frac{\partial c_n^\beta}{\partial t} = \bar{D}^\beta \text{Li}^+ \frac{\partial^2 c_n^\beta}{\partial x_n^2} + \frac{\partial c_n^\beta}{\partial x_n} \frac{x_n}{\xi} \frac{d\xi}{dt}$$

c_n^β ; the concentration at the n th grid point

$$(0 < x_n < \xi, n=2,3,\dots,r-1)$$

x_n ; the position of the n th grid point

- change of concentration gradients across the phase α

$$\frac{\partial c_n^\alpha}{\partial t} = \bar{D}^\alpha \text{Li}^+ \frac{\partial^2 c_n^\alpha}{\partial x_n^2} + \frac{\partial c_n^\alpha}{\partial x_n} \frac{L - x_n}{L - \xi} \frac{d\xi}{dt}$$

ξ ; the location of the α/β phase boundary

$c_{\beta\alpha}$; the concentrations close to the phase

boundary on the phase β side

$$(\xi < x_n < L, n=r+1, r+2, \dots, N)$$

$c_{\alpha\beta}$; the concentrations close to the phase

boundary on the phase α side

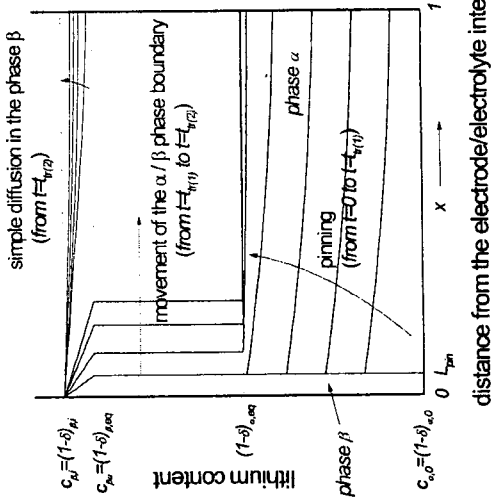
- flux balance at the α/β phase boundary for lithium ion

$$(c_{\beta\alpha} - c_{\alpha\beta}) \frac{d\xi}{dt} = \bar{D}^\alpha \left(\frac{\partial c}{\partial x} \right)_{x=\xi^+} \text{Li}^+ - \bar{D}^\beta \left(\frac{\partial c}{\partial x} \right)_{x=\xi^-} \text{Li}^+$$

- W.D.Murray and F.Landis, *Trans. ASME Ser.D* 81 (1959) 106.

Theory of Three-stage Current Transient

* From a standpoint of flux balance, the phase boundary is pinned at the location, $x=L_{pin}$, close to the electrode/electrolyte interface **until the flux entering the phase boundary** $J_{\beta\alpha} (= -\bar{D}^{\beta} \frac{\partial c^{\beta}}{\partial x} \Big|_{x=\xi^-})$ **exceeds that flux leaving the phase boundary** $J_{\alpha\beta} (= -\bar{D}^{\alpha} \frac{\partial c^{\alpha}}{\partial x} \Big|_{x=\xi^+})$. \implies “pinning”



* **Potentiostatic lithium injection into the electrode subjected to the ‘pinning’ limitation and the impermeable constraint**

- Initial Condition (I.C.)

$$c = c_{\beta,i} - (c_{\beta,i} - c_{\beta\alpha}) \frac{x}{L_{pin}}, \quad \text{for } 0 < x \leq L_{pin} \quad \text{at } t=0$$

$$c = c_{\alpha,0}, \quad \text{for } L_{pin} < x < L \quad \text{at } t=0$$

- Boundary Condition (B.C.)

$$c = c_{\beta,i}, \quad \text{for } x=0 \quad \text{at } t>0$$

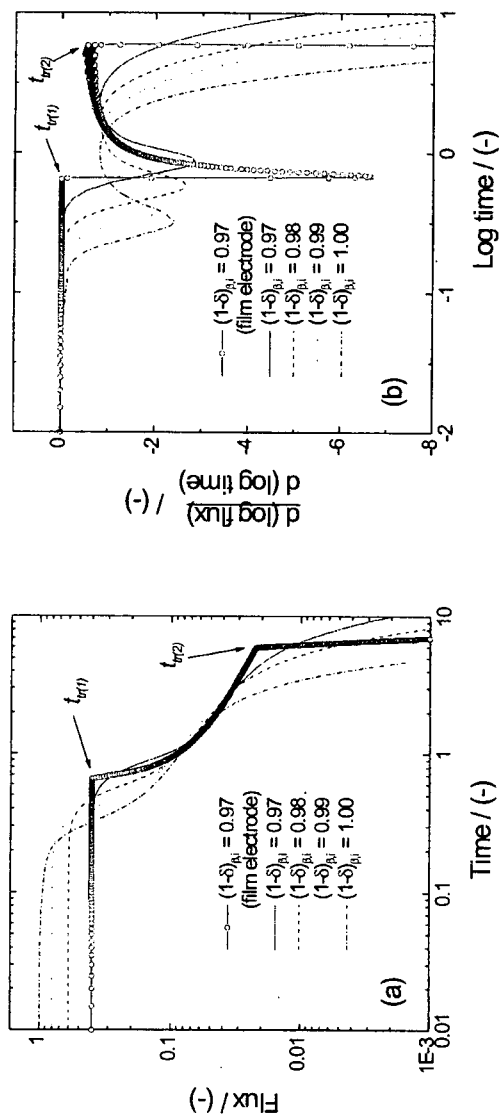
$$\frac{\partial c}{\partial x} = 0, \quad \text{for } x=L \quad \text{at } t>0$$

- Y.-M. Choi, S.-I. Pyun and J. M. Paulsen, *Electrochim. Acta* 44(4) (1998) 623.

- H.-C. Shin and S.-I. Pyun, press in *Electrochim. Acta* (1998).

Numerical Analysis of Three-stage Current Transient

The first, second and third stages of the simulated transients and the derivatives corresponds well to those stages of the lithium content profile which indicate the 'pinning' of the phase boundary, the PBM and lithium intercalation into the single β phase, respectively.

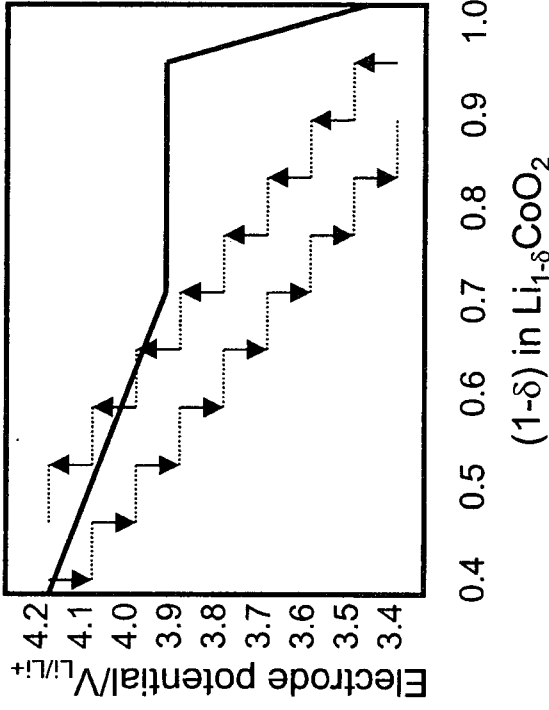


(a) Simulated build-up current transient on a logarithmic scale and (b) the derivative of the logarithmic current transient obtained from the film electrode with the equilibrium stoichiometry $(1-\delta)_{\beta,i}$ of 0.97 and from the porous electrode with various equilibrium stoichiometries. The distribution of the oxide particle size was assumed to obey a normal distribution with unity as the mean and 0.2 as the standard deviation.

Potentiostatic Current Transient Technique

2. Small potential step condition

- initial potential :
4.2 $V_{\text{Li/Li}^+}$ for the lithium intercalation
- 3.4 $V_{\text{Li/Li}^+}$ for the lithium deintercalation
- potential step : 50 / 100 $\text{mV}_{\text{Li/Li}^+}$
= driving force for the lithium intercalation and deintercalation



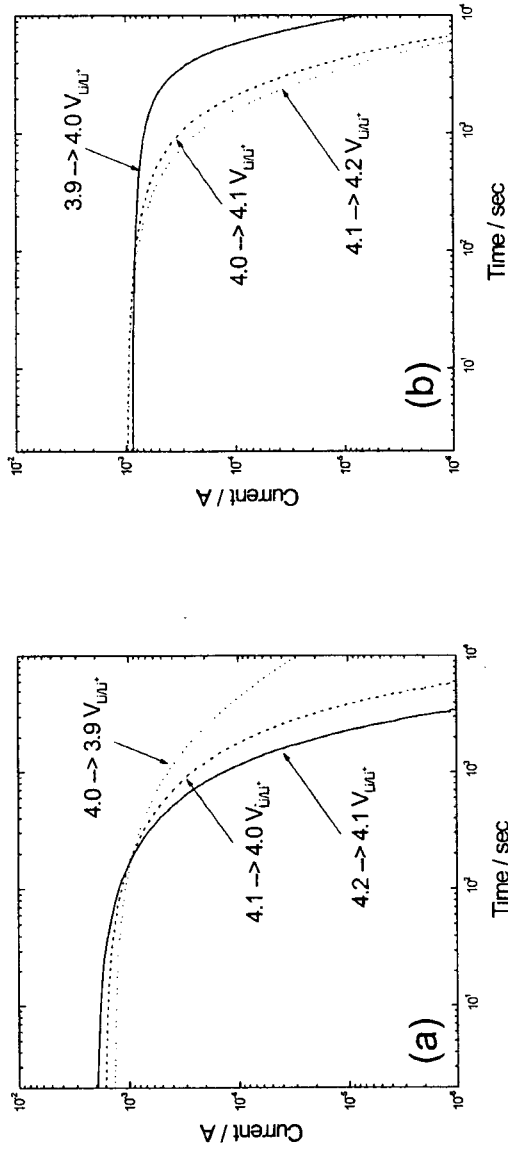
concentration gradient < electrical potential(galvani potential) gradient

Under a **small potential step condition**, we can distinguish the contribution of the **electric field to the lithium transport through the oxide electrode** from that contribution of the **lithium ion diffusivity**

Two-stage Current Transient

The current values at the first stage of the decay transient were nearly constant irrespective of the lithium extraction potential in α -phase region

⇒ The lithium transport through the $\text{Li}_{1-\delta}\text{CoO}_2$ oxide during the lithium deintercalation is mainly impeded by the electric field across the oxide electrode generated by the electron-depleted space charge layer



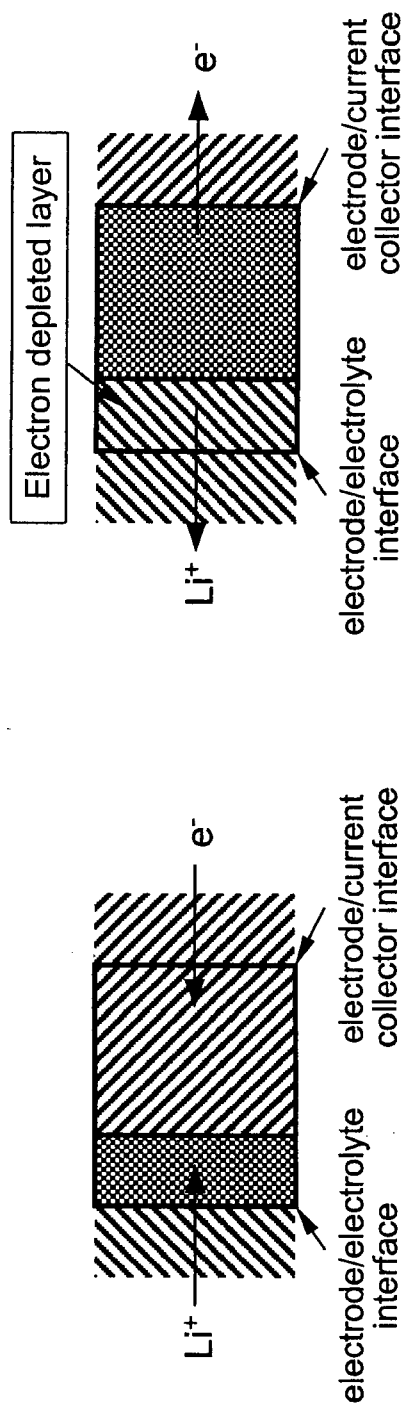
(a) Current build-up and (b) decay transients in logarithmic scale, obtained from the porous $\text{Li}_{1-\delta}\text{CoO}_2$ electrodes in 1 M LiClO_4 propylene carbonate solution under the application of small potential steps, 100 mV.

Electric Field effect on lithium transport

If the electronic conductivity \gg the lithium ion conductivity

← As the deintercalation proceeds, the transition of the semiconductor to metal occurs

⇒ The electron-depleted space charge layer can conceivably be formed beneath the electrode/electrolyte interface during the lithium deintercalation from the electrode at low lithium content, i.e., α -phase



Numerical Analysis on Fickian Diffusion

Fick's second law

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$

Non-dimensionalization

let $x/l \rightarrow \xi$; dimensionless distance

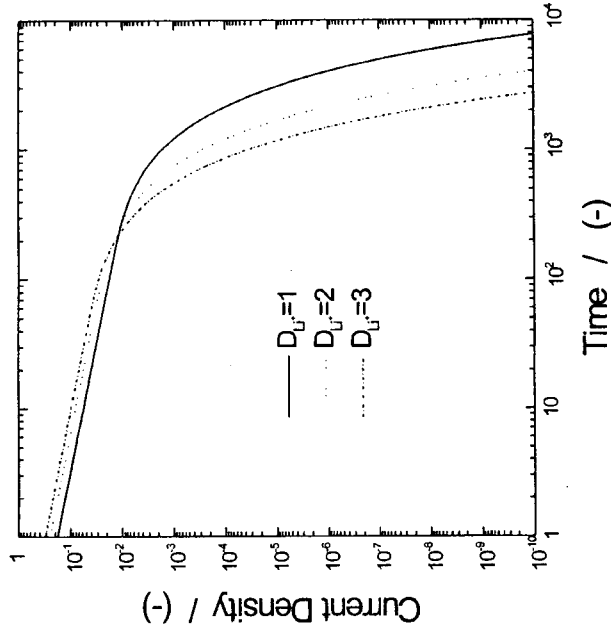
$c/c_0 \rightarrow u$; dimensionless concentration

$Dt/l^2 \rightarrow \tau$; dimensionless time

$$\Rightarrow \frac{\partial^2 u}{\partial \xi^2} = \frac{\partial u}{\partial \tau}$$

Numerical solution

$$\begin{aligned} u(i, j+1) &= \frac{\Delta \tau}{(\Delta \xi)^2} (u(i+1, j) - 2u(i, j) + u(i-1, j)) + u(i, j) \\ j(N, j) &= \frac{u(N, j) - u(N-1, j)}{\Delta \xi} \end{aligned}$$



Current build-up transients in logarithmic scale for the Fickian diffusion in the electrode numerically simulated with various chemical diffusivities

Future Works

- I. *Effects of Phase Transformation, Electric Field and Intercalation-induced Stress on Lithium Transport through $\text{Li}_{1-\delta}\text{CoO}_2$ Film electrode for Thin-film Rechargeable Lithium Battery*
- II. *Numerical Analysis on the Lithium Transport involving Phase Boundary Movement through Composite and Film Electrodes for Rechargeable Lithium Battery*
- III. *Effects of Cation Mixing and Electric Field on Electrochemical Lithium Intercalation into $\text{Li}_{1-\delta}\text{M}_y\text{Ni}_{1-y}\text{O}_2$ (M=Al, Co, Mn) Composite Electrodes for Rechargeable Lithium Battery*
- IV. *Electrochemical Lithium Intercalation into $\text{Li}_{1\pm\delta}\text{Mn}_{2-y}\text{M}_y\text{O}_4$ (M=Ni, Co, Cr...) Composite and Film Electrodes for Rechargeable Lithium Battery*