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Electrochemical Reduction of Rare Earth Oxides (Nd_2O_3, La_2O_3) via Co-reduction of NiO in LiCl Molten Salt

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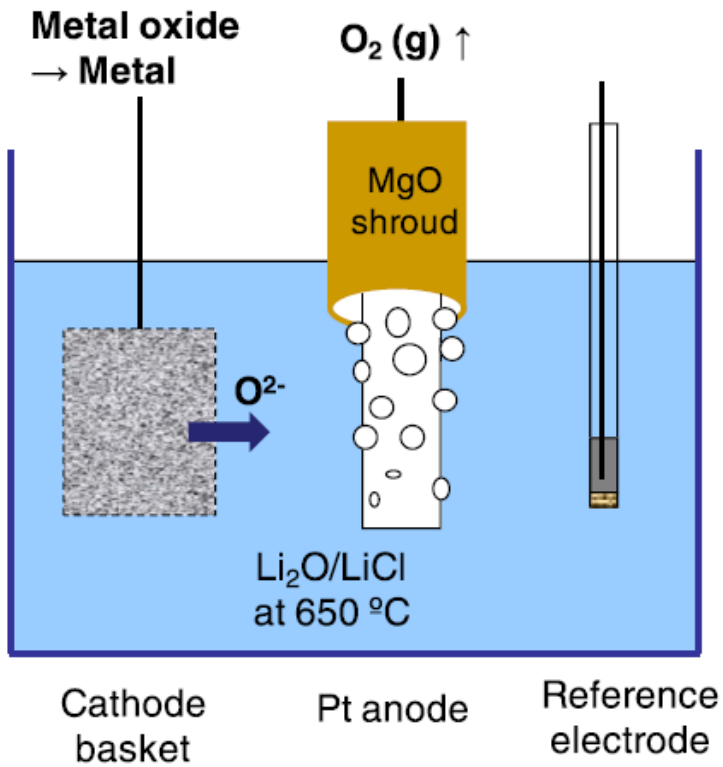
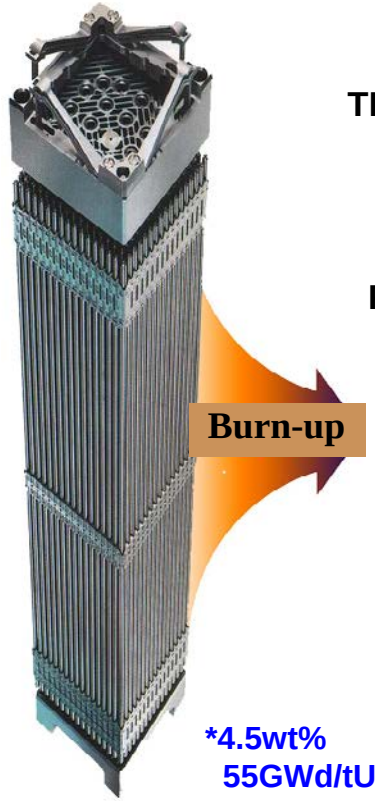
Electrochemical reduction



- Oxide feed contained in metal cathode basket
- LiCl salt with ~1.0 wt% Li_2O at 650°C
- Cathode: Reduction
  $M_xO_y + xe- \rightarrow M + yO^{2-}$
- Anode: Oxidation
  $2O^{2-} \rightarrow O_2(g) + 4e^-$ (inert anode)
  $C + 2O^{2-} \rightarrow CO_2(g) + 4e^-$ (carbon anode)

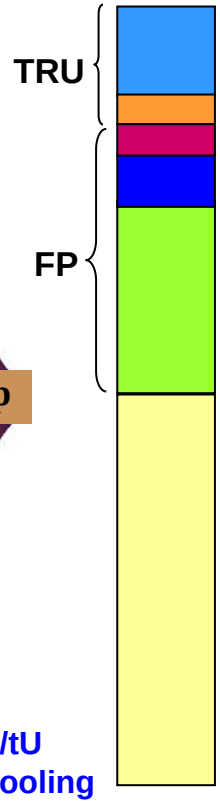
Rare earth oxides in SNF



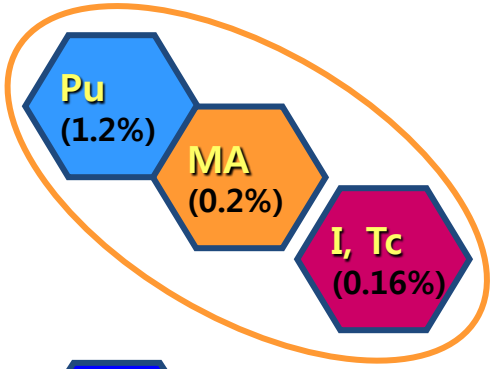
Burn-up

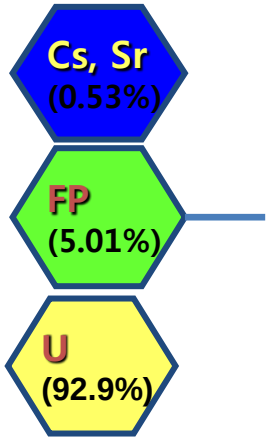
*4.5wt%
55GWd/tU
10 yrs cooling

Fresh fuel(100% Uranium)



Spent fuel





RE : 1.7%
NM: 1.3%
Others

Reported reducibility of RE oxides

Literature	Reduction degree of Nd_2O_3	Feed
Herrmann et al. (2007) J. Nucl. Sci. Technol.	< 10 %	BR3 spent fuel
Barnes and Williams(2008) 2nd IPRC	< 50 %	Oxide pellet sintered at 2050°C
Jeong et al. (2008) Electrochimica Acta	< 10 %	Mixed oxide powder sintered at 1200°C
Choi et al. (2012) Chem. Eng. J.	< 50 %	Porous SIMFUEL granule sintered at 1700°C
Park et al. (2012) J. Chem. Eng. Japan	< 20 %	Chemical rxn. (Nd_2O_3+Li at LiCl salt)

Chemistry of Rare Earth Oxide with UCl_3

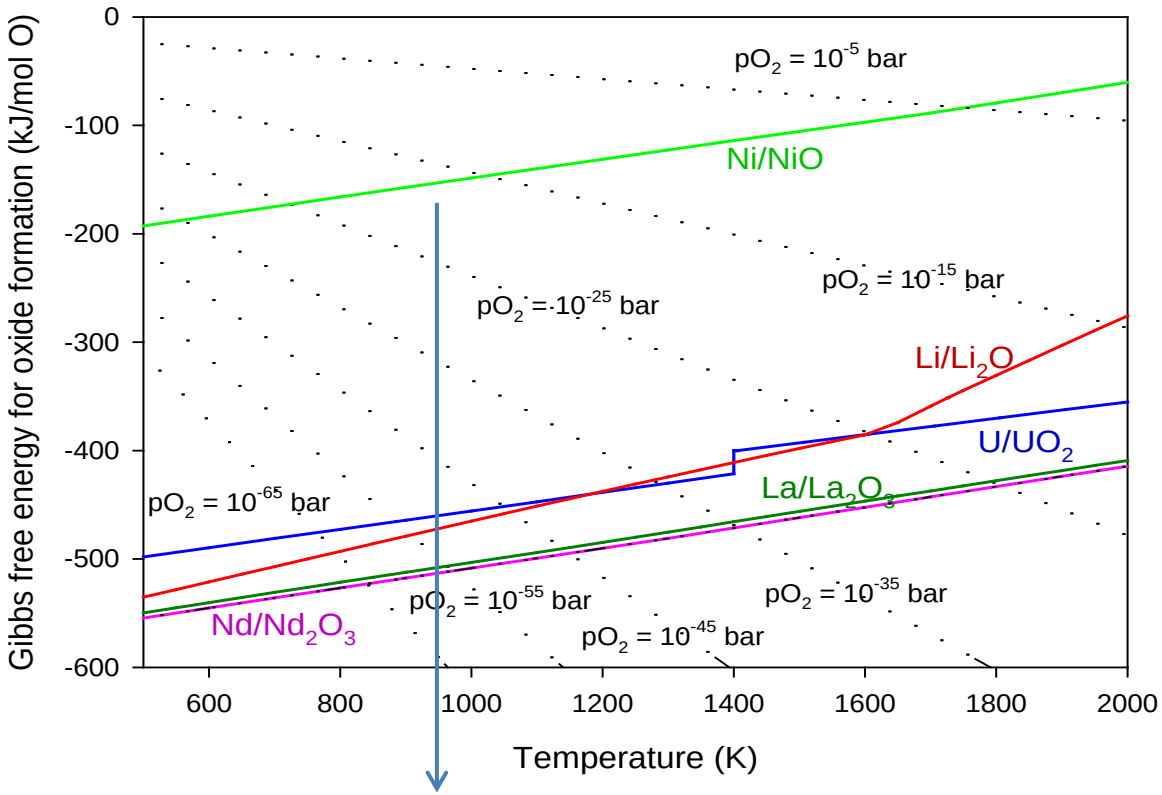
- Chemical rxns between rare earth oxide and UCl_3:

$$3Nd_2O_3 + 2UCl_3 = 6NdOCl + UO_2 + UO \quad \Delta G^0 = -98.630 \text{ kcal.}$$

$$Nd_2O_3 + 2UCl_3 = 2NdCl_3 + UO_2 + UO \quad \Delta G^0 = -37.855 \text{ kcal.}$$

- Contaminate the eutectic salt with fine UO_X powder
- Decrease of UCl_3 concentration in the electrorefining process

Thermodynamic consideration



923 K (650 °C)

Decomposition voltage at 650 °C

E^0 (V)

0	$O^{2-}/O_2(g)$
-0.8	Ni^{2+}/Ni
-2.4	U^{4+}/U
-2.47	Li^{+}/Li
-2.64	La^{3+}/La
-2.67	Nd^{3+}/Nd

Li metal is deposited before reduction of RE

$\Delta G°_{rxn}$ for chemical reaction

Reaction	$\Delta G°_{rxn}$ (650°C), kJ	Theoretical max. Li_2O concentration (wt%)*
$Nd_2O_3 + 6Li(l) = 2Nd + 3Li_2O(l)$	175	0.005
$La_2O_3 + 6Li(l) = 2La + 3Li_2O(l)$	160	0.01
$Y_2O_3 + 6Li(l) = 2Y + 3Li_2O(l)$	264	0.0001
$Sm_2O_3 + 6Li(l) = 2Sm + 3Li_2O(l)$	183	0.004
$UO_2 + 4Li(l) = U + 2Li_2O(l)$	10.7	Solubility limited
$NiO + 2Li(l) = Ni + Li_2O(l)$	-302	

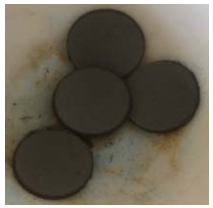
* γ_{Li2O} calculated to be 0.19

Concept for RE_2O_3 reduction

- Electrochemical reduction of RE oxides via co-reduction of NiO
- Thermal synthesis of perovskite-like structure A2BO4 or spinel structure AB2O4 ($NiNd_2O_4$) and perovskite ABO3 ($LaNiO_3$)
- Good electric conductivity and fast lattice diffusion of oxygen with such compounded oxides
- Ni ions (octahedral site) starts to be reduced. Lattice oxygen diffuses through oxygen vacancies to near Ni (octahedral site).

Experimental

Cathode electrode



Nd:Ni (1:5 mol ratio) or
La:Nd:Ni (1:1:10 mol ratio)

↓

Hand Mixing (10 min)

↓

Pressing (200 bar)

↓

Pellet

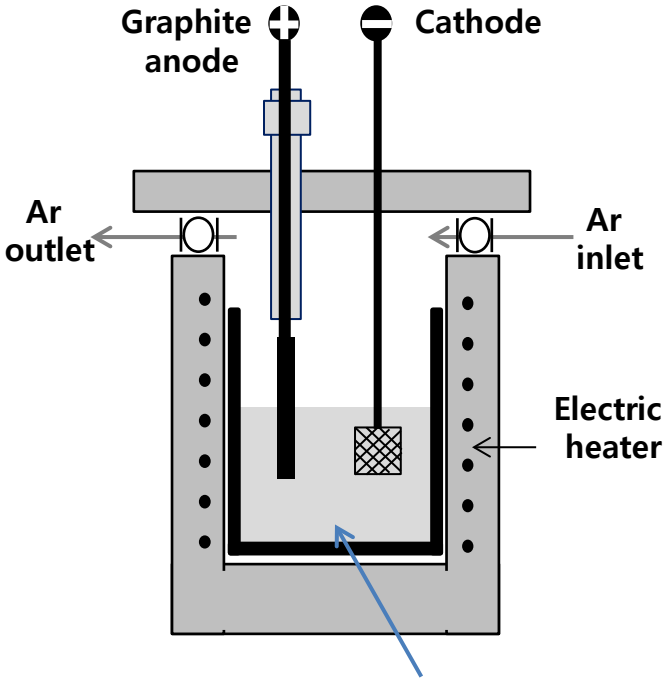
↓

Sintering

↓

Electrochemical Reduction

Electrolysis cell



LiCl molten salt

(650 or 750°C)

<mixed oxides pellet>

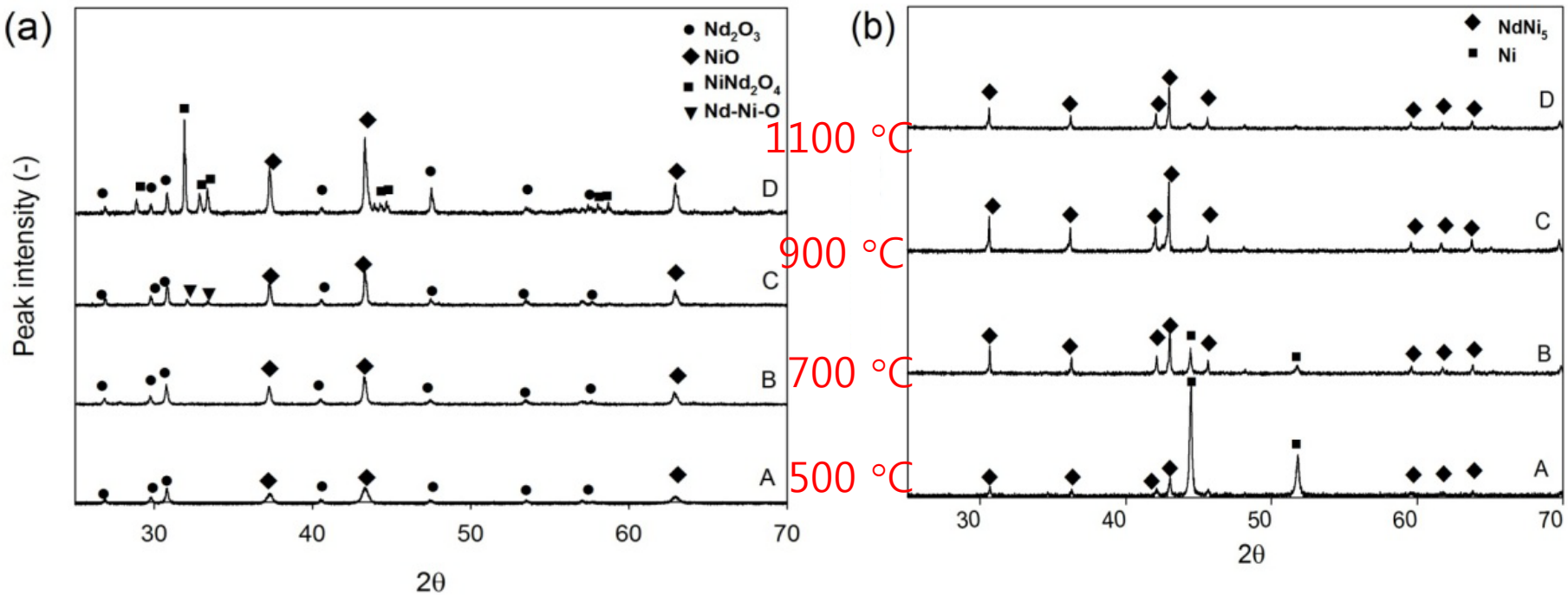
Electrochemical reduction →

<Product: $NdNi_5$,$La_{0.5}Nd_{0.5}Ni_5$ >

<Cathode>

Effect of thermal treatment

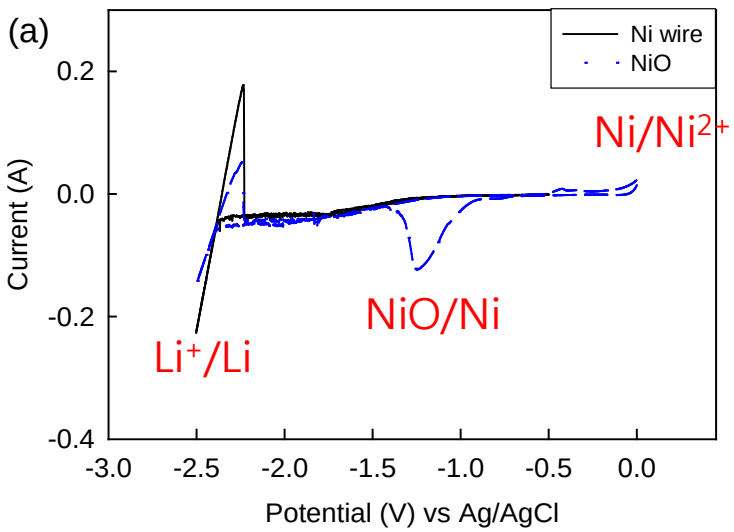
- Calcination temperature of mixed oxide: 500, 700, 900 and 1100 °C
- Experimental condition: LiCl at 750 °C, 1-h electrolysis at 3.2 V
- Calcination temperature is an important factor for reduction of Nd_2O_3.

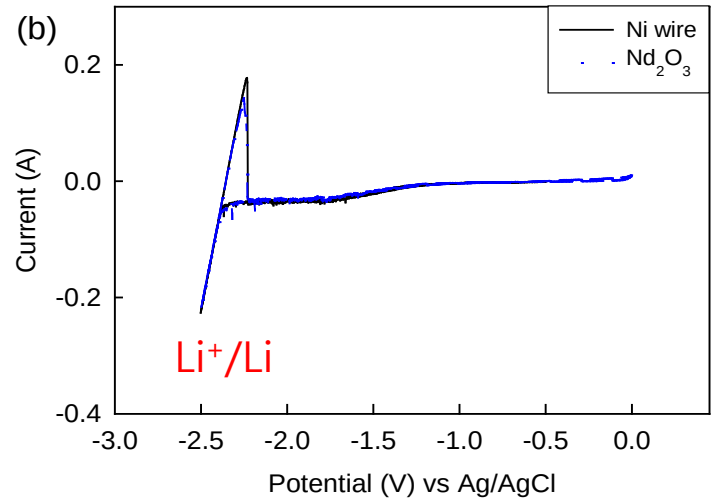


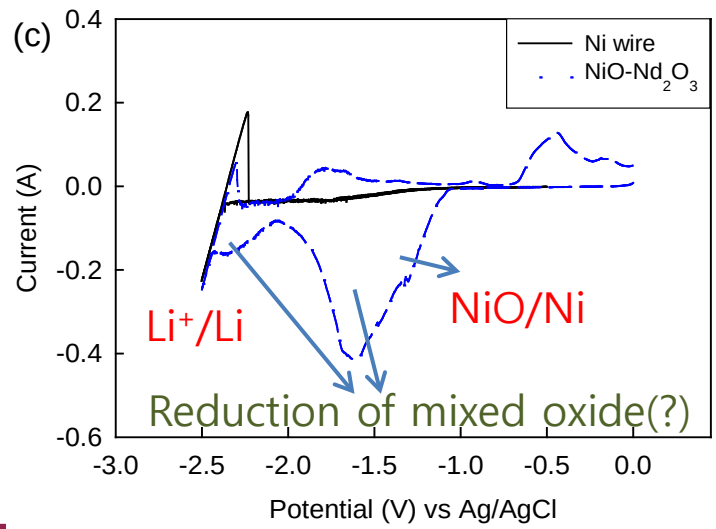
Before electrolysis

After electrolysis

Cyclic voltammetry

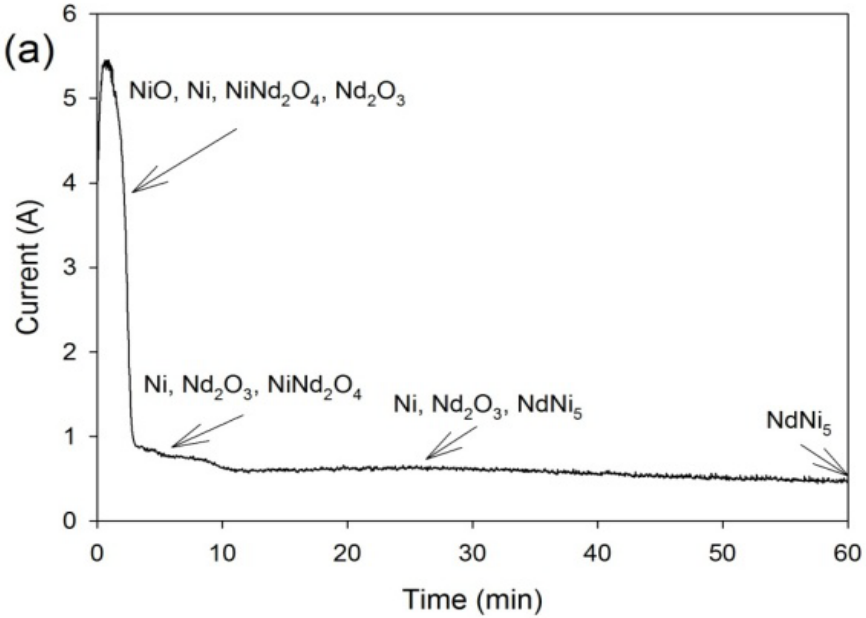


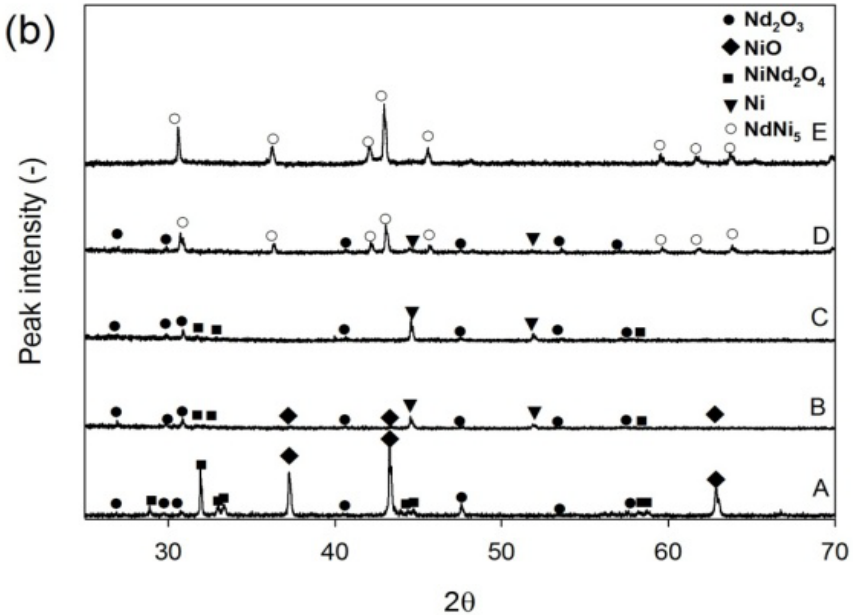




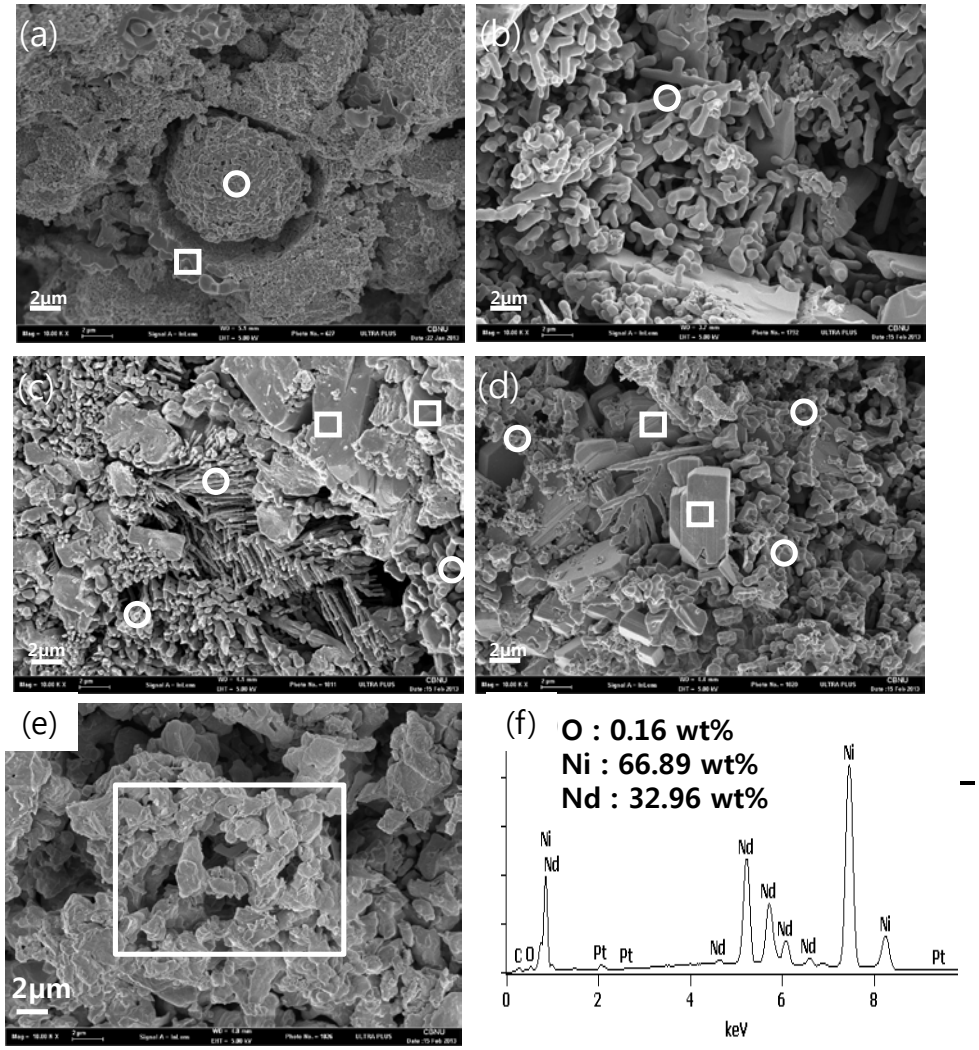
Intermediate products-XRD

- Nd_2O_3-NiO mixed oxide (calcined at 1100 C) was reduced at 3.2 V in LiCl (750 °C) in the preliminary test.
- Nd_2O_3 can be completely reduced via co-reduction of NiO within 1h.
- Intermetallic compound of $NdNi_5$ is produced after electrolysis.





Intermediates-SEM-EDS analysis



(a) 0%, (b) 50%, (c) 100%,

(d) 150%, and (e) 200%

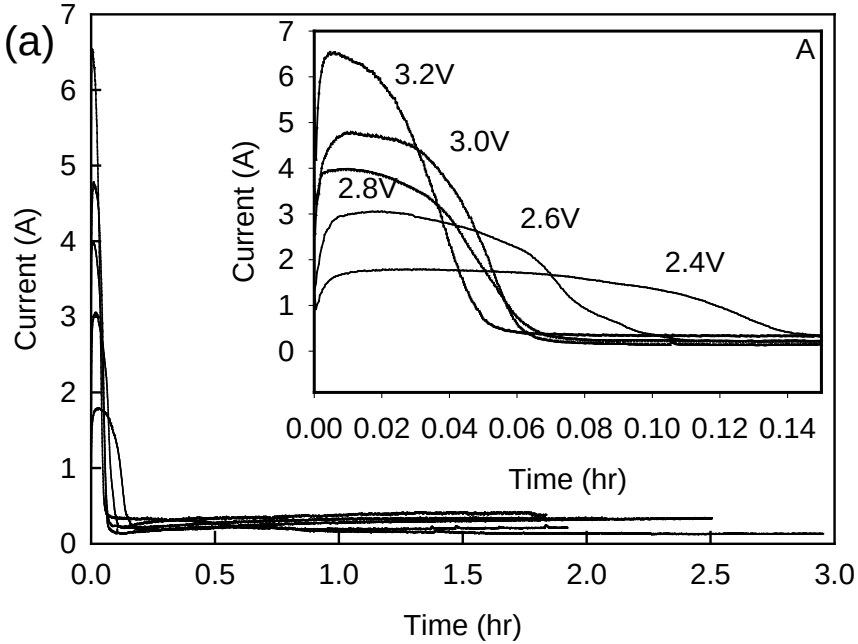
(f) EDS analysis of (e).

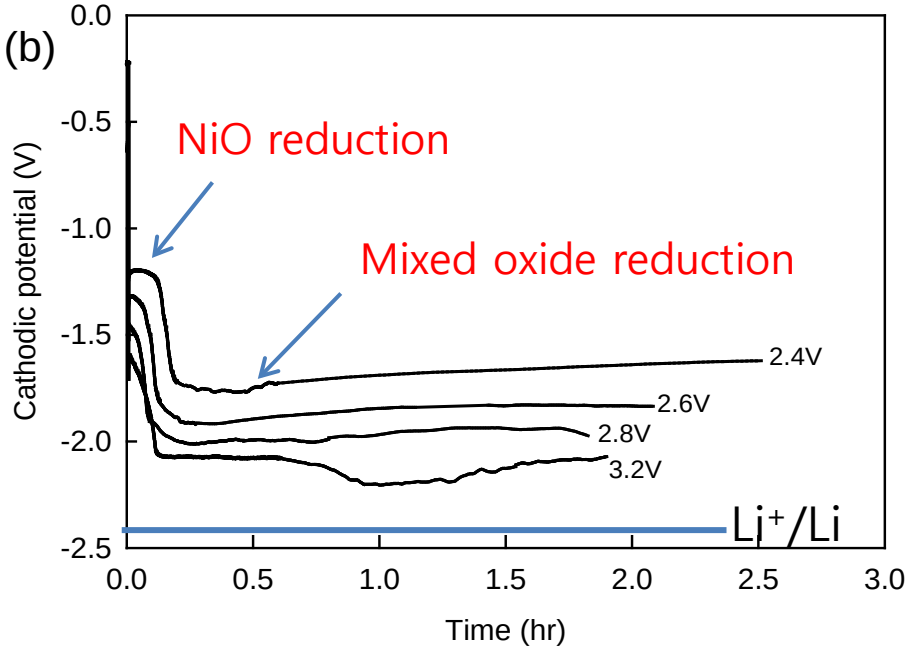
○ - Ni rich phase
□ - Nd rich oxide phase

- Final product contains 1,600 ppm Oxygen (EDS).

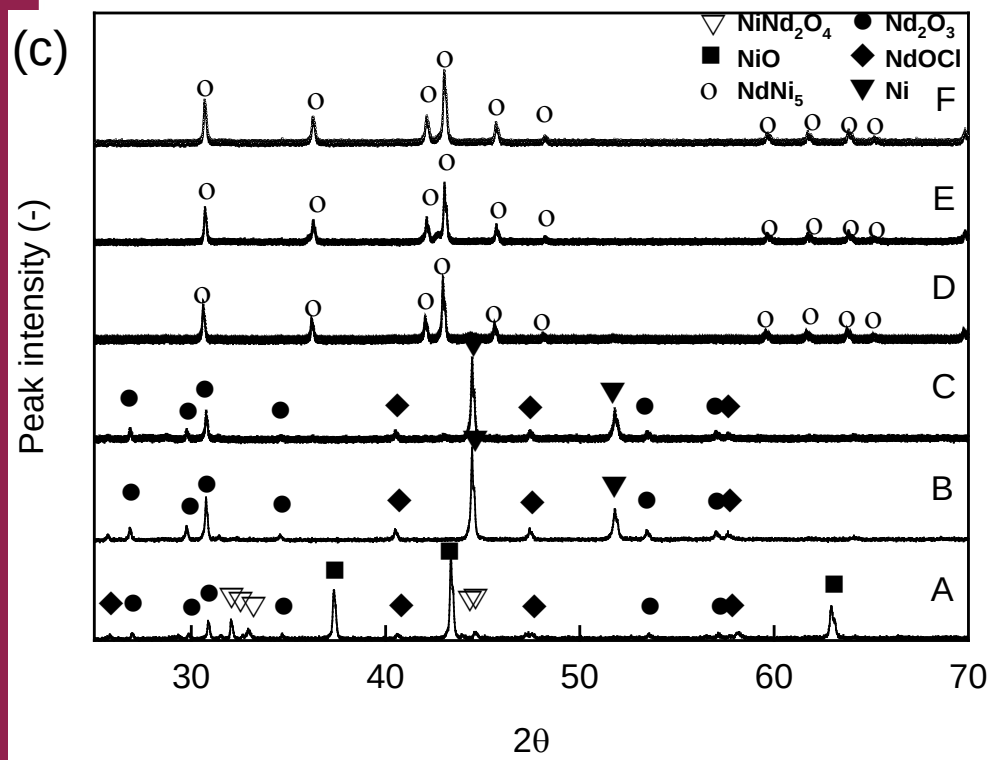
Constant voltage electrolysis

- Experimental condition: LiCl at 650 °C, 200 % of theoretical charges
- Measured cathodic potentials are more positive than the Li^+/Li potential → possibly NiO (initiation) and $NiNd_2O_4$ (propagation by lattice diffusion of oxygen) aided direct reduction





Product analysis



V_{cell}

3.2 V

3.0 V

2.8 V

2.6 V

2.4 V

Mixed oxide feed

Nd reduction via co-reduction with Ni

Ni reduction only

Electrode reaction path

- Cathodic reaction:

$NiO + 2e^- \rightarrow Ni + O^{2-}$

$NiNd_2O_4 + 2e^- \rightarrow Ni + O^{2-} + Nd_2O_3$

fast & easy at a lower potential

$10Ni + Nd_2O_3 + 6e^- \rightarrow 2NdNi_5 + 3O^{2-}$

$9Ni + NiNd_2O_4 + 8e^- \rightarrow 2NdNi_5 + 4O^{2-}$

Lattice diffusion of oxygen in the perovskite-like structure

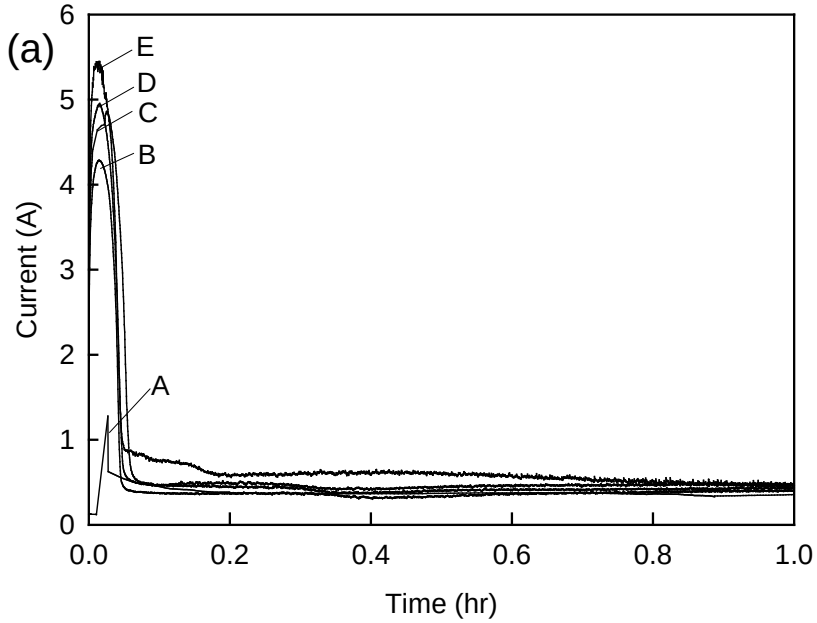
$5Ni + NdOCl$ (if any) $+ 3e^- \rightarrow NdNi_5 + O^{2-} + Cl^-$

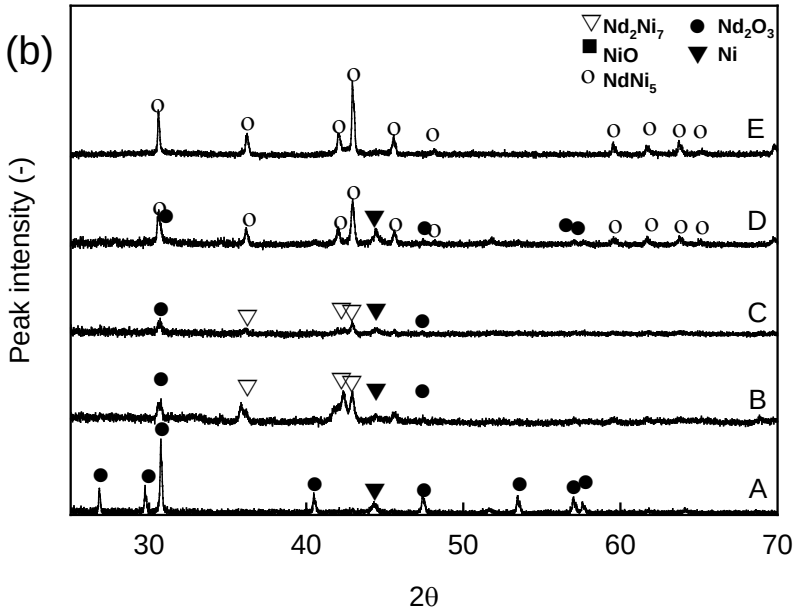
- Anodic reaction:

$C + xO^{2-} \rightarrow CO_X(g) + 2xe^-$

Effect of Nd:Ni ratio

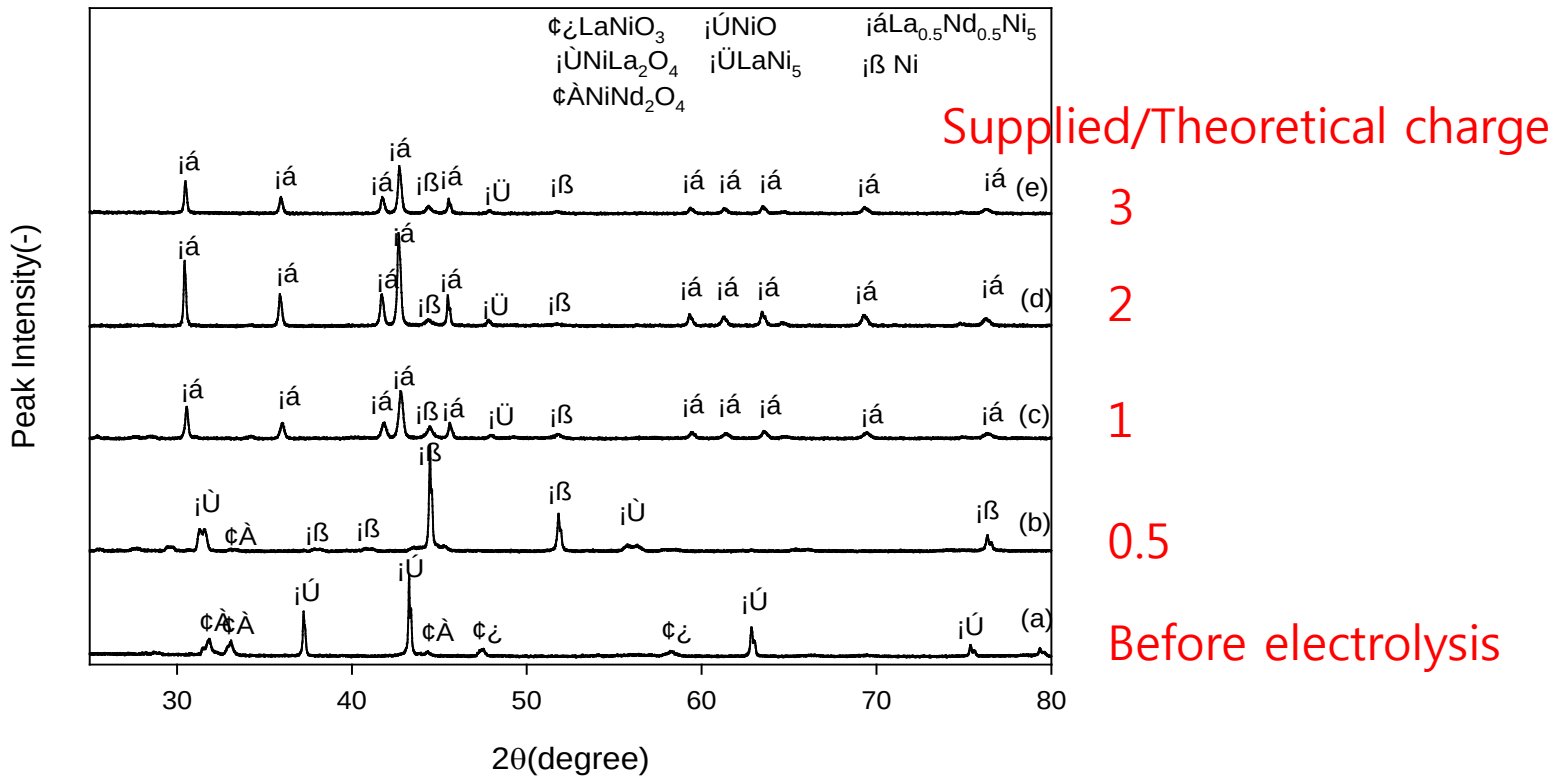
- Experimental condition: 3.2 V, 200% of the theoretical charges at 650°C
- Nd:Ni ratio: (A) 1:1, (B) 1:2, (C) 1:3, (D) 1:4, and (E) 1:5
- $NdNi_{3.5}$ and $NdNi_5$ are observed as final products with different Nd:Ni ratio. Nd_2O_3 exists below the ratio of 1:4.





Reduction of La_2O_3-Nd_2O_3-NiO

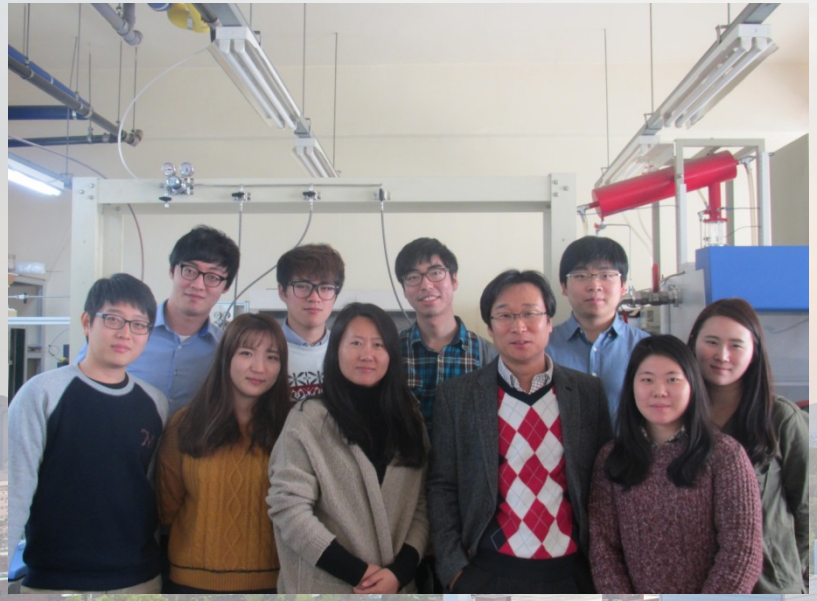
- La_2O_3-Nd_2O_3-NiO ternary mixed oxide (La:Nd:Ni = 0.5:0.5:5)
- La_2O3 and Nd_2O3 are successfully reduced in LiCl molten salt.



Summary & Future work

- Reducibility of Rare earth oxide (Nd_2O_3 and La_2O_3) has been tested via co-reduction with NiO.
- The presence of $NiNd_2O_4$ and $LaNiO_3$ (perovskite or perovskite-like) in the mixed oxide pellet leads to the fast reduction of rare earth oxide.

Following studies are necessary:

- Effect of Li_2O concentration in LiCl salt
- UO_X-RE_2O_3-NiO feed test

Thank you for your attention