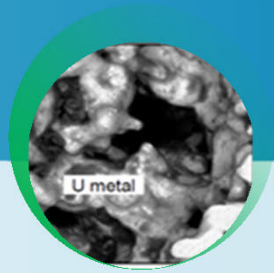
A Boron Doped Diamond Electrode as an Inert Anode for Electrolytic Reduction of UO_2



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Contents

I Introduction

- Pt & graphite electrode
- Carbon vs. BDD

II Experimental approach

- Characteristics of BDD electrode
- Experimental conditions

III Results and discussion

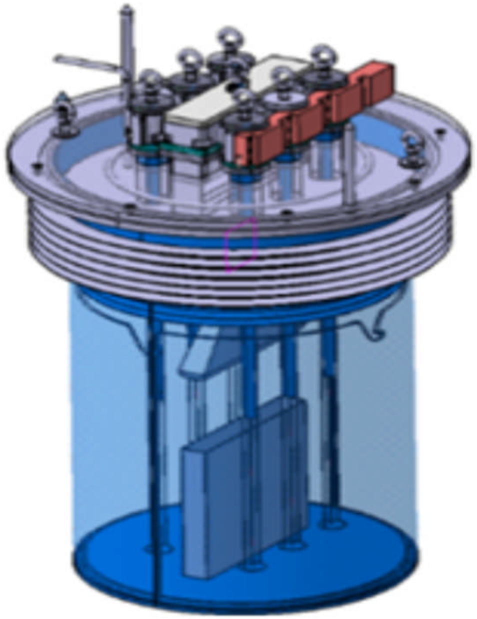
- Electrode potential & polarization curves
- C/A ratio & electrolytic reduction
- Stability of BDD electrode

IV Conclusions

- BDD as an inert anode (C/A ratio < 0.63)
- Enhancement of current density (must-do)

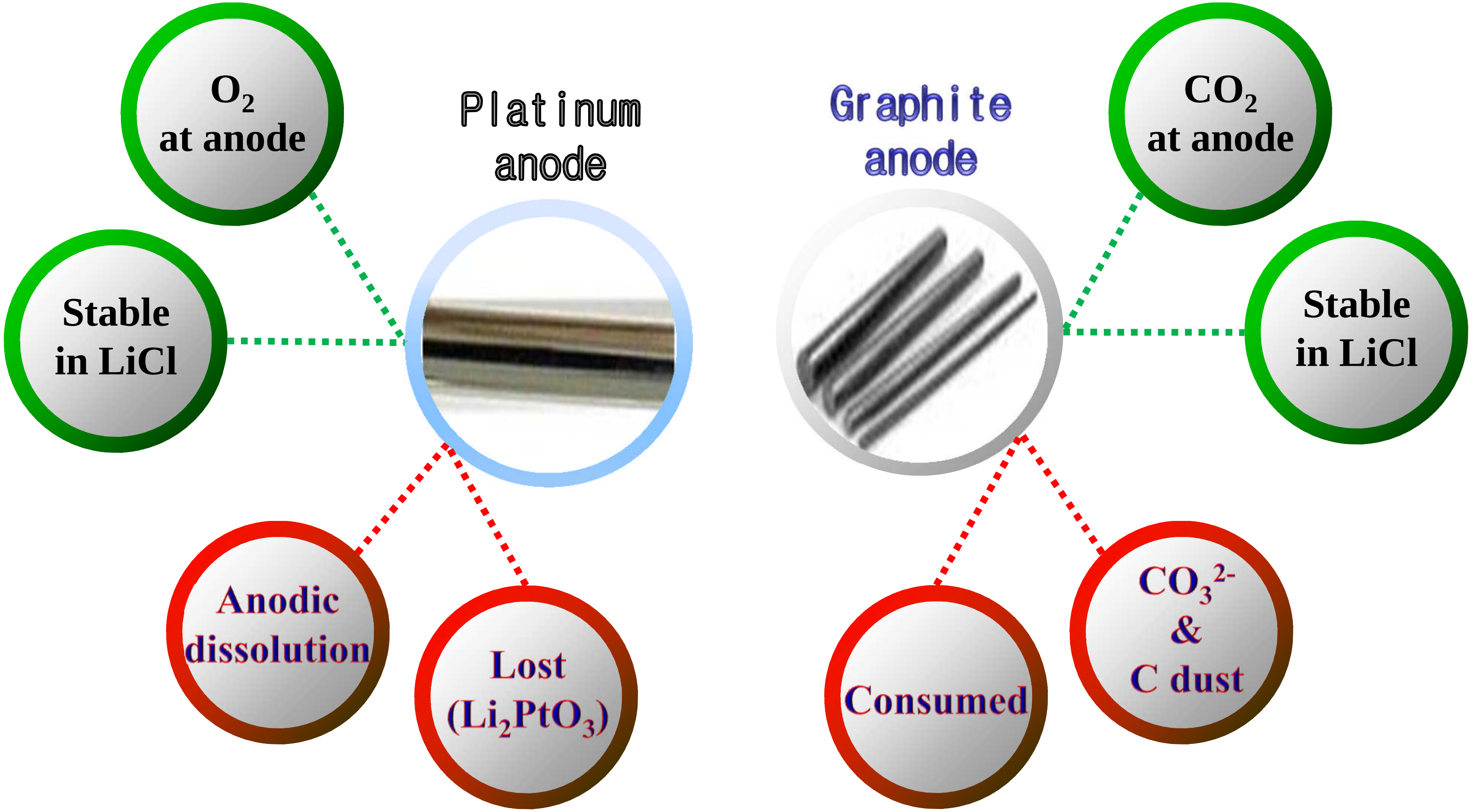
I Introduction

Electrolytic Reduction Process for UO_2



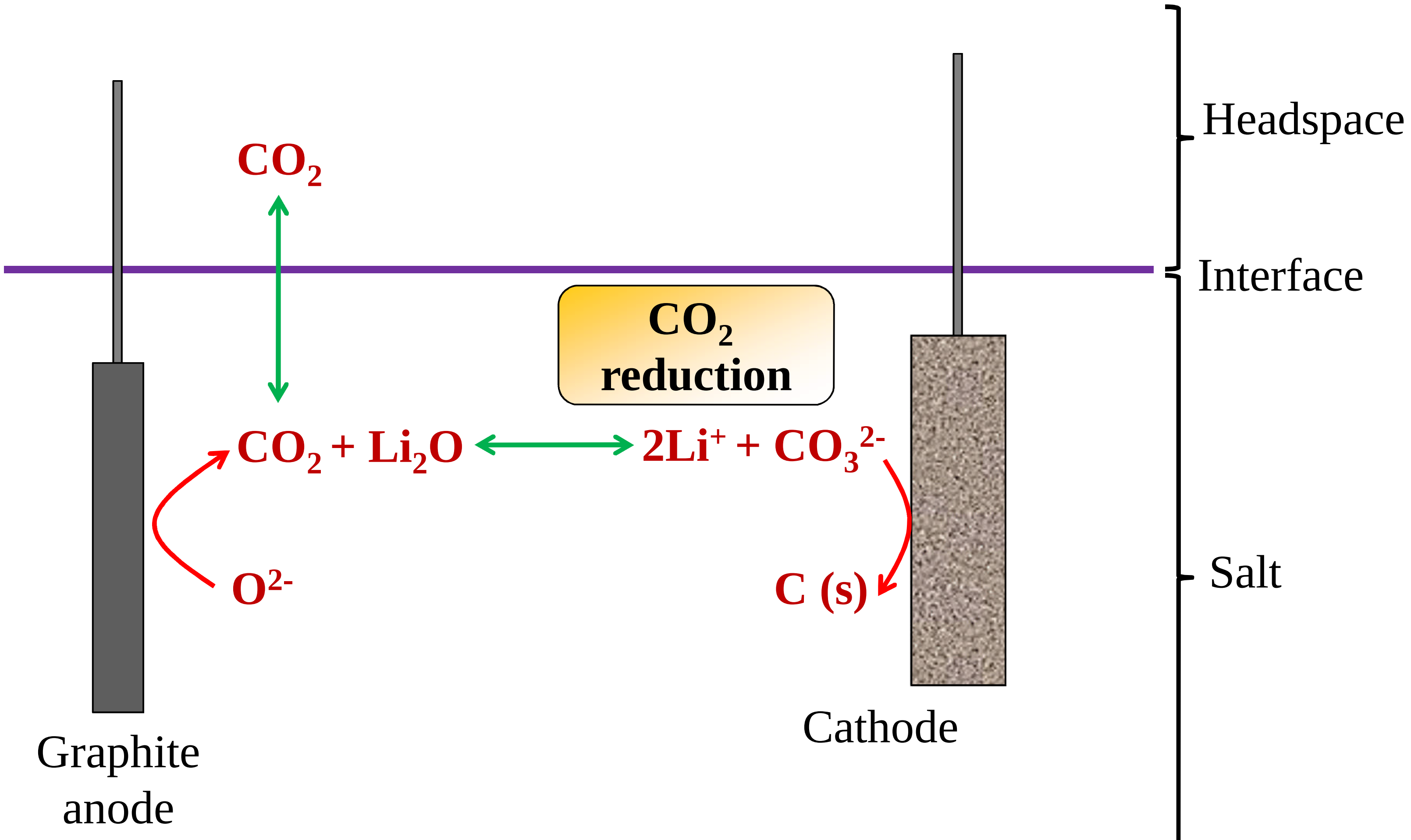
- Anode : $2O^{2-} \rightarrow O_2 + 4e^-$ (Pt)
  $C + 2O^{2-} \rightarrow CO_2 + 4e^-$ (C)
- Cathode: $4Li^+ + 4e^- \rightarrow 4Li$
  $UO_2 + 4Li \rightarrow U + 2Li_2O$
- 650°C, 1 wt% Li_2O–LiCl molten salt

Encountered Problems of Pt & C Anodes



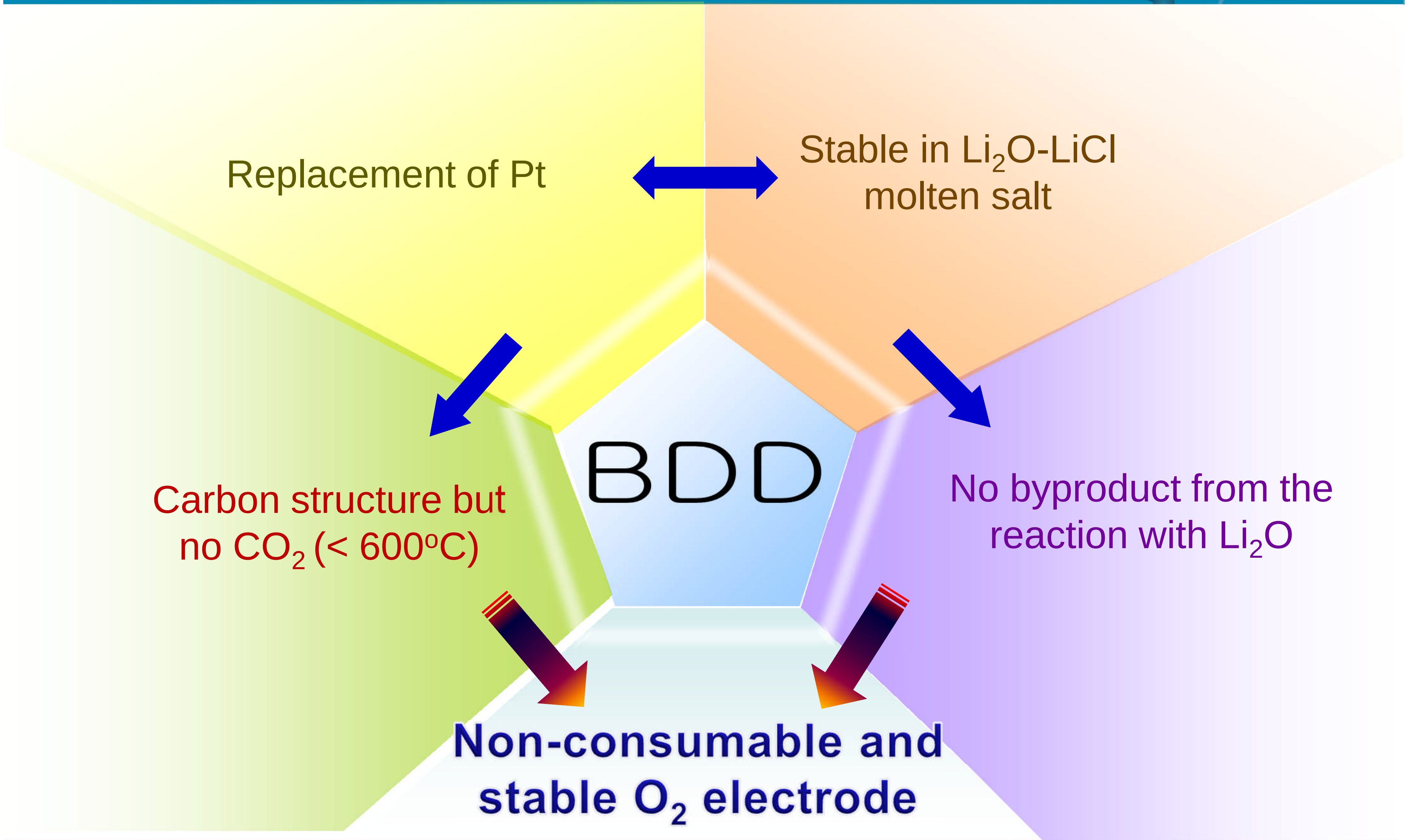
- Replacement of Pt with graphite ➔ not a good option

Carbon Deposition on the Cathode

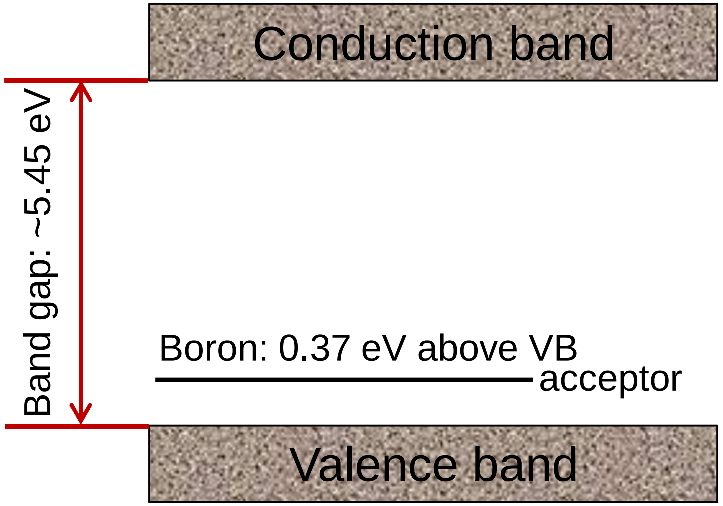


- Removing 100% of CO_2 ➔ O.K. (possible?)
- No CO_2 ➔ O.K. (But, 650°C enough to burn graphite)

Boron Doped Diamond (BDD)



BDD as a semiconductor



* Diamond: insulator

* BDD: p-type semiconductor

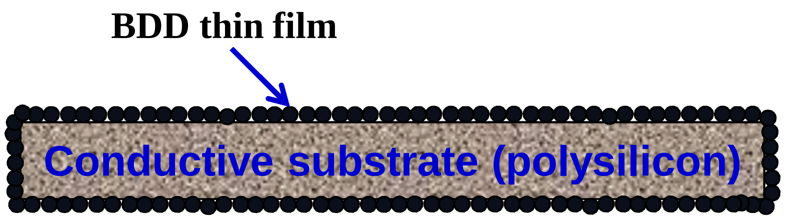
[A. Kraft, 2007]

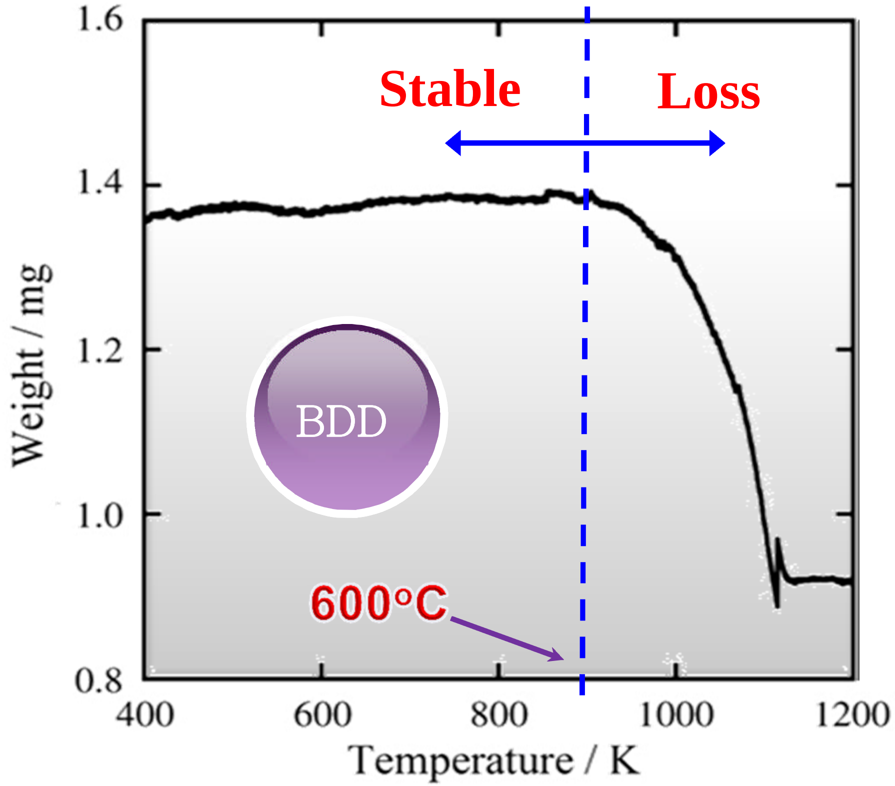
II Experimental Approach

Characteristics and Operation Temperature

- Substrate: polysilicon

  (1 cm W x 10 cm L x 0.3 cm T)
- Dopant conc.: 5,000 ppm
- Film thickness: 2~3 μm
- Method: CVD





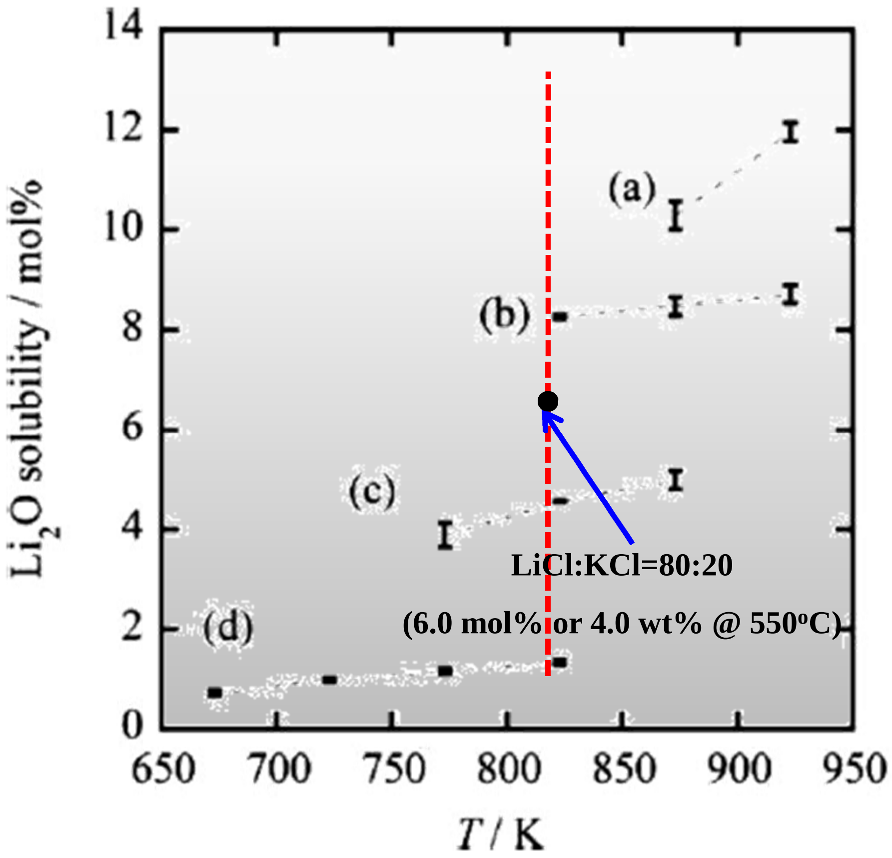
[Kado et al., 2009]

❖ **Operation temperature < 600°C**

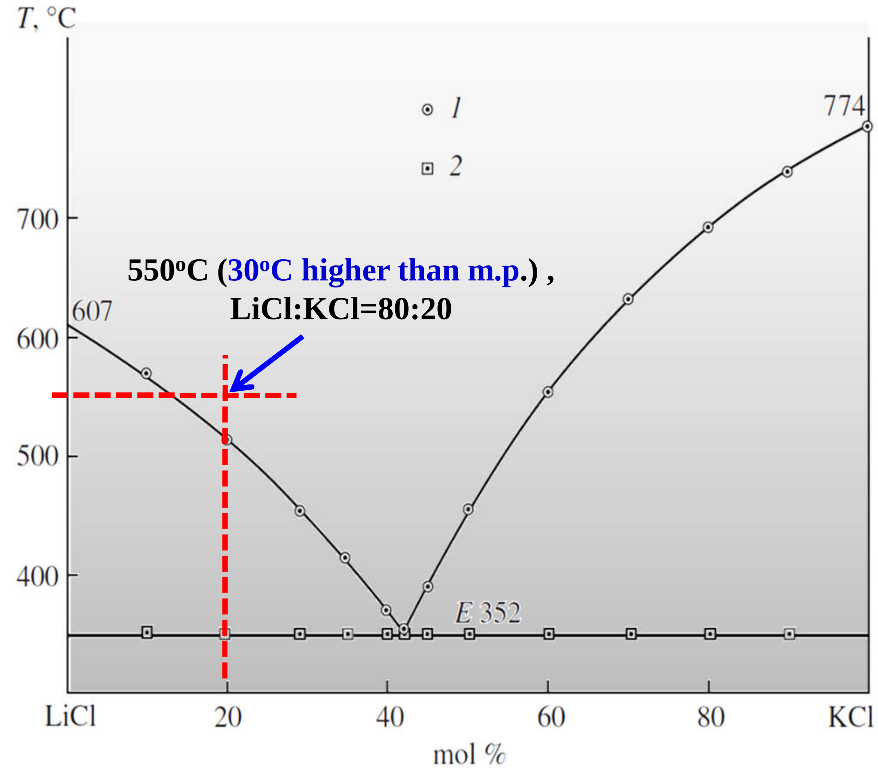
❖ **550°C in this study**

$T_{ignition}$ of Diamond, °C (K)
720~800 (993~1073) (O_2) 850~1000 (1123~1273) (Air)

Salt Selection (Mixture of LiCl and KCl)



a. 100:0, b. 90:10, c. 75:25, d. 58.5:41.5. [Kado et al., 2008]



[Basin et al., 2008]

❖ 1 wt% Li_2O-LiCl-KCl (LiCl:KCl = 80 : 20) ← $T_{operation}$ & Li_2O solubility

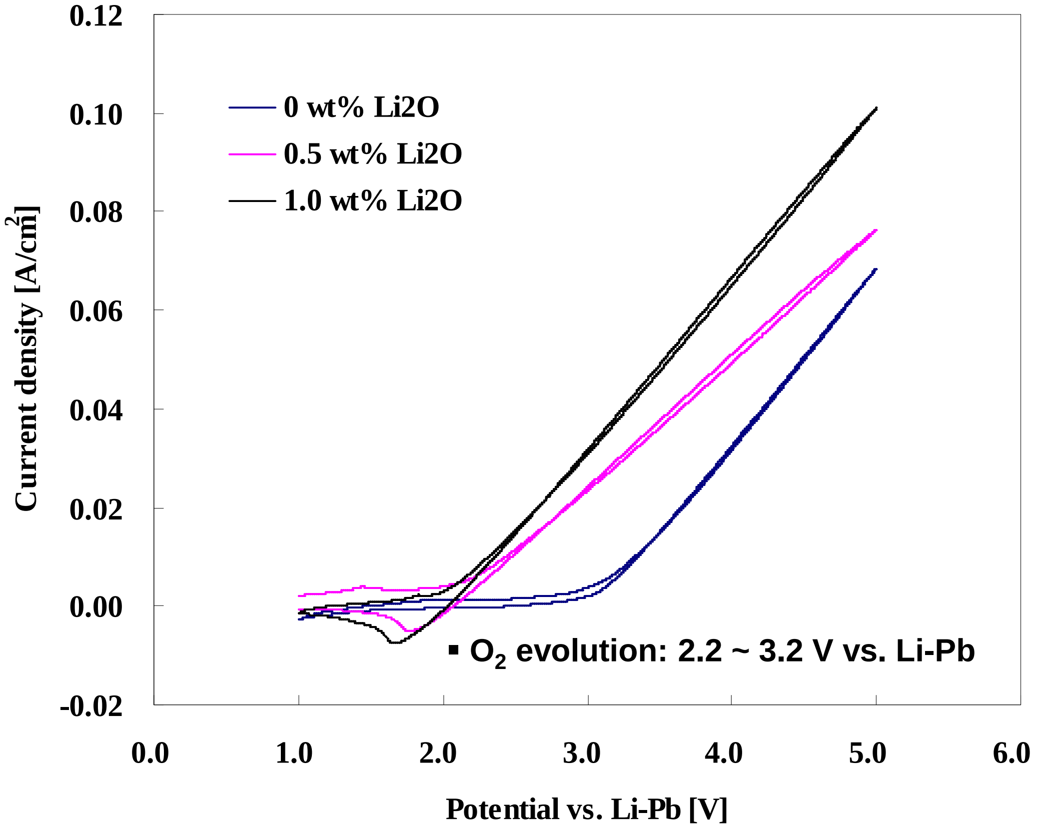
Experiments

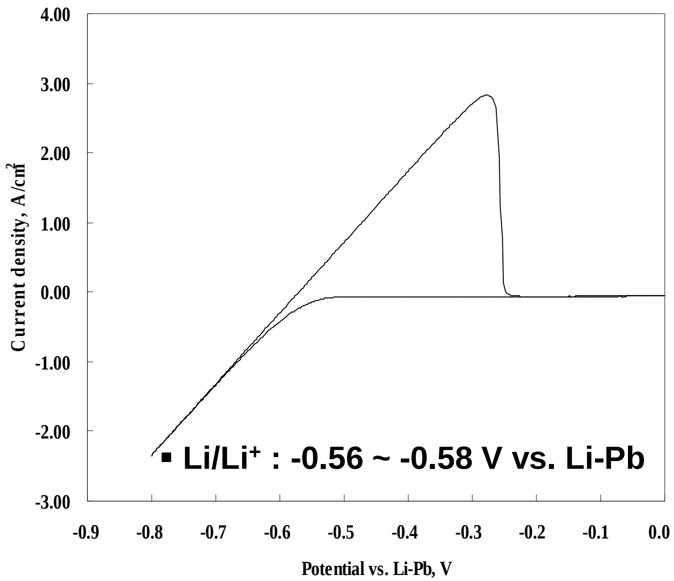
1 wt% Li_2O-LiCl-KCl (80:20) @550^oC

- Cyclic voltametry & Polarization curves
- C/A ratio & UO_2 reduction
- BDD characterization

III Results and Discussion

Cyclic Voltammograms @ 550°C

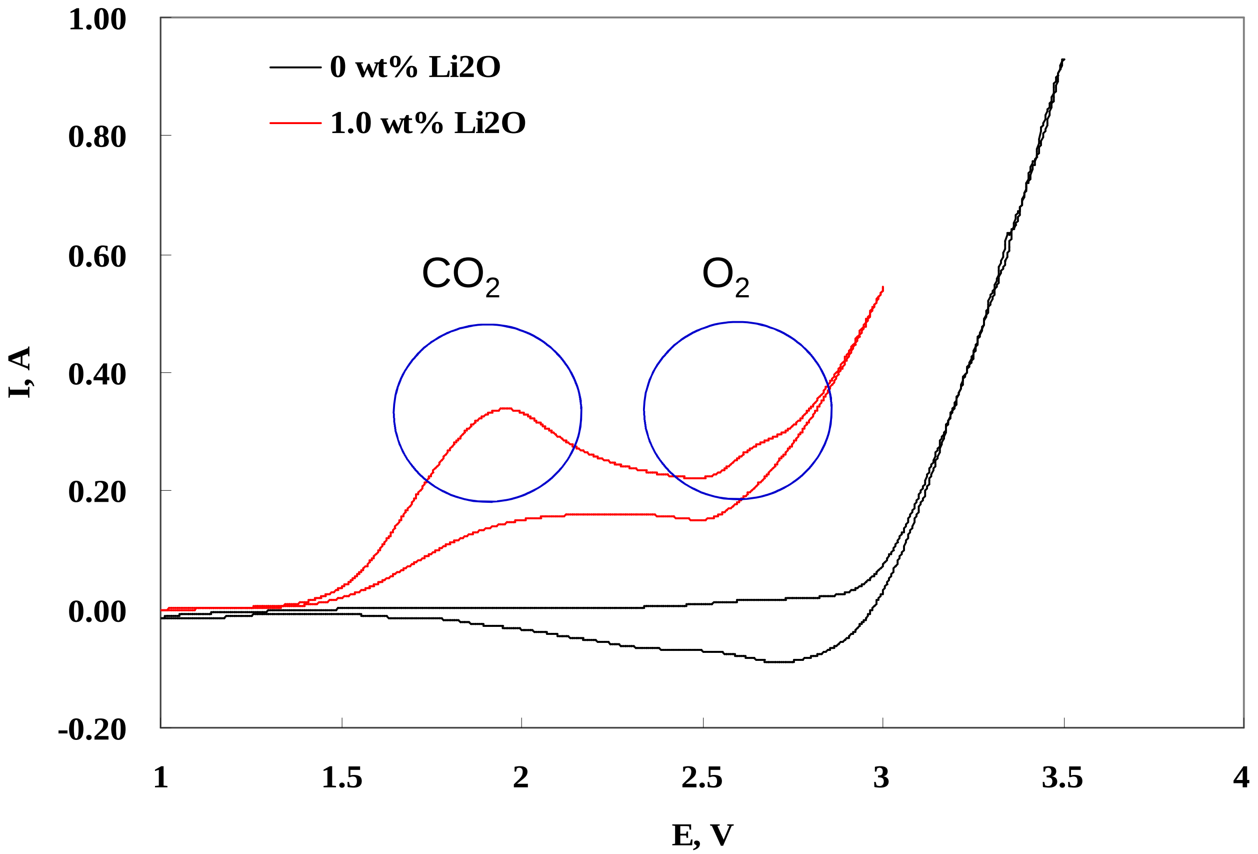


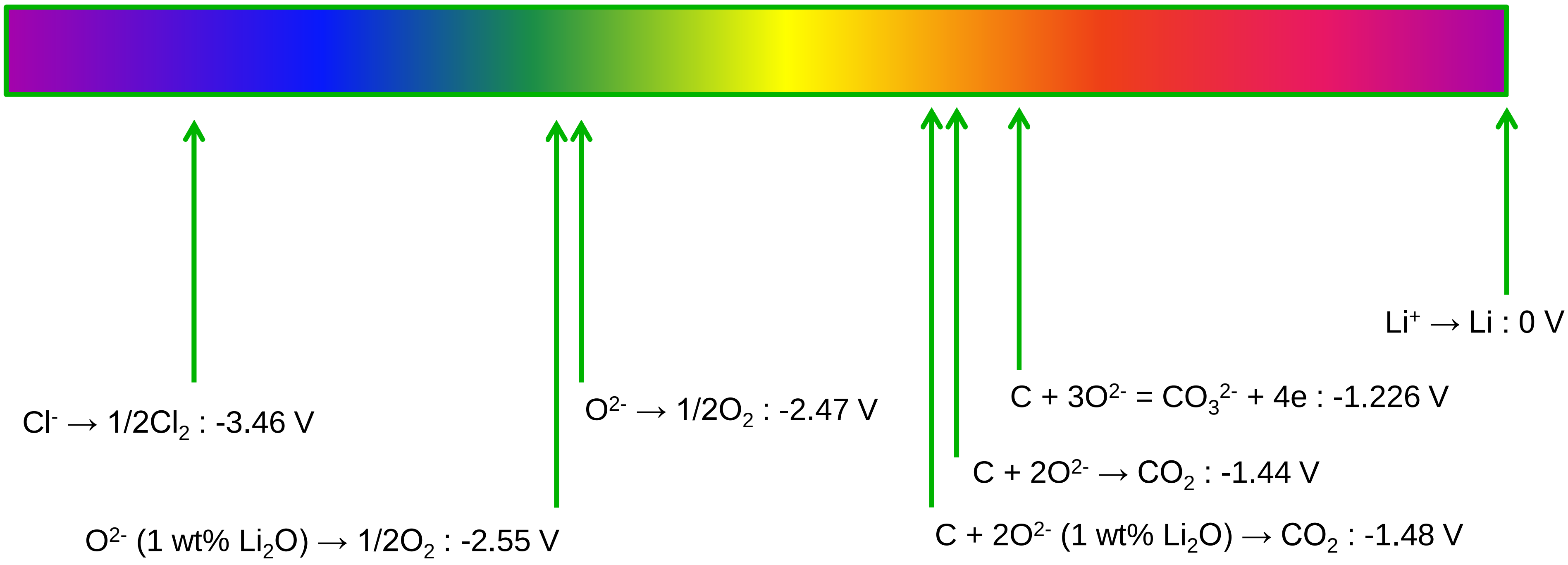


CV w/ STS-316 rod

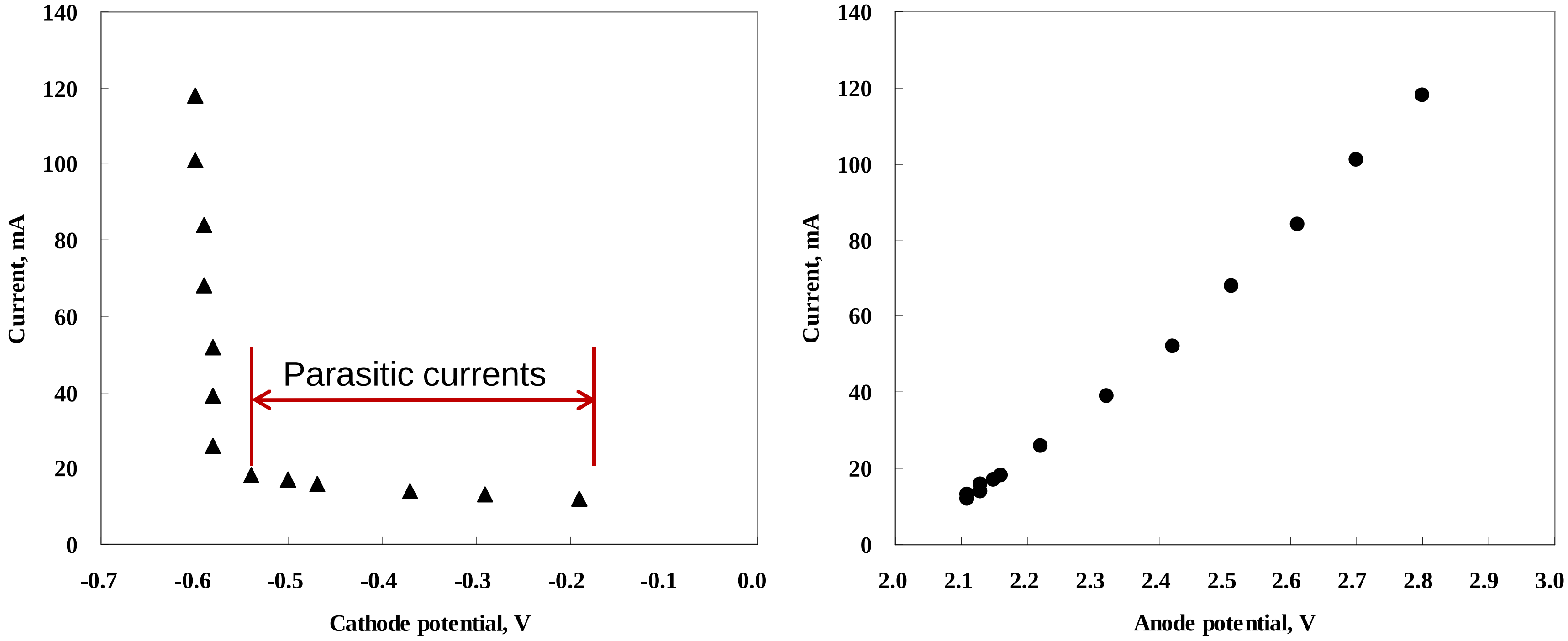
- **Recommendable cell voltage = approximately 2.8 ~ 3.8 V**

An Example of CV of a Graphite Electrode



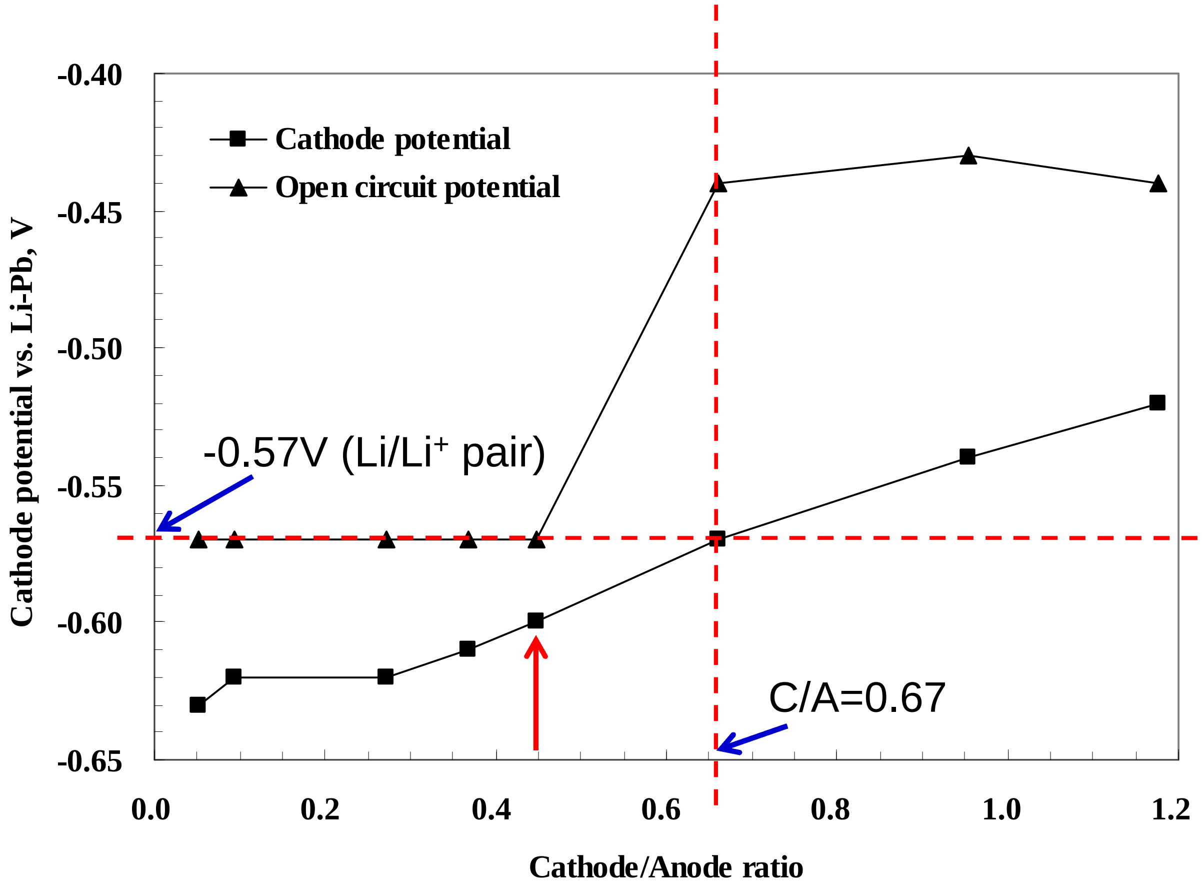

Cl⁻ → 1/2Cl₂ : -3.46 V
O²⁻ (1 wt% Li₂O) → 1/2O₂ : -2.55 V
O²⁻ → 1/2O₂ : -2.47 V
C + 2O²⁻ (1 wt% Li₂O) → CO₂ : -1.48 V
C + 2O²⁻ → CO₂ : -1.44 V
C + 3O²⁻ = CO₃²⁻ + 4e : -1.226 V
Li⁺ → Li : 0 V

Polarization Curves

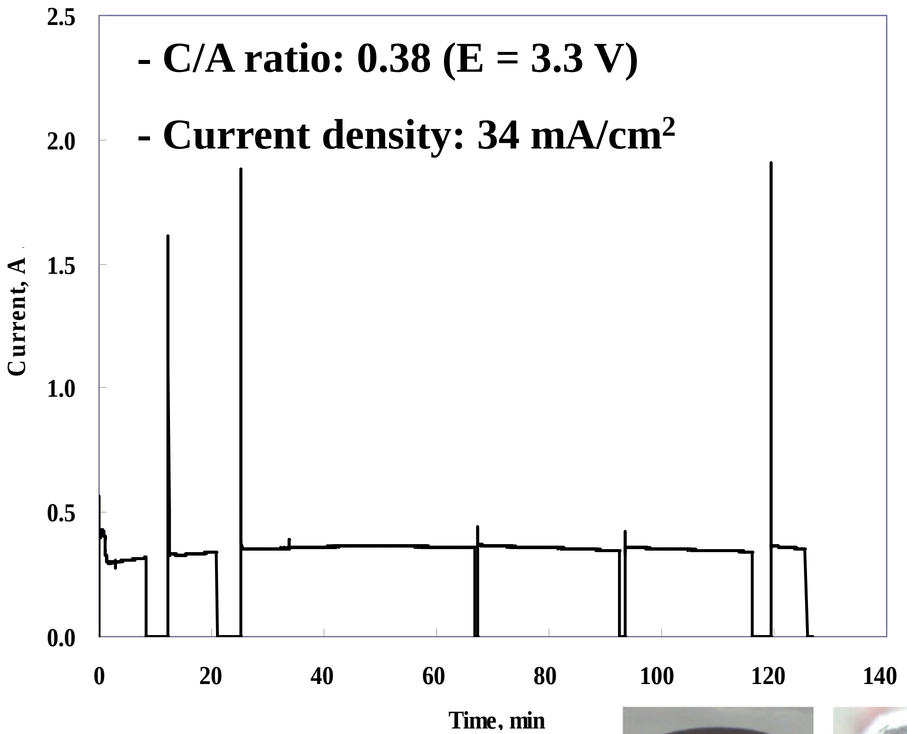


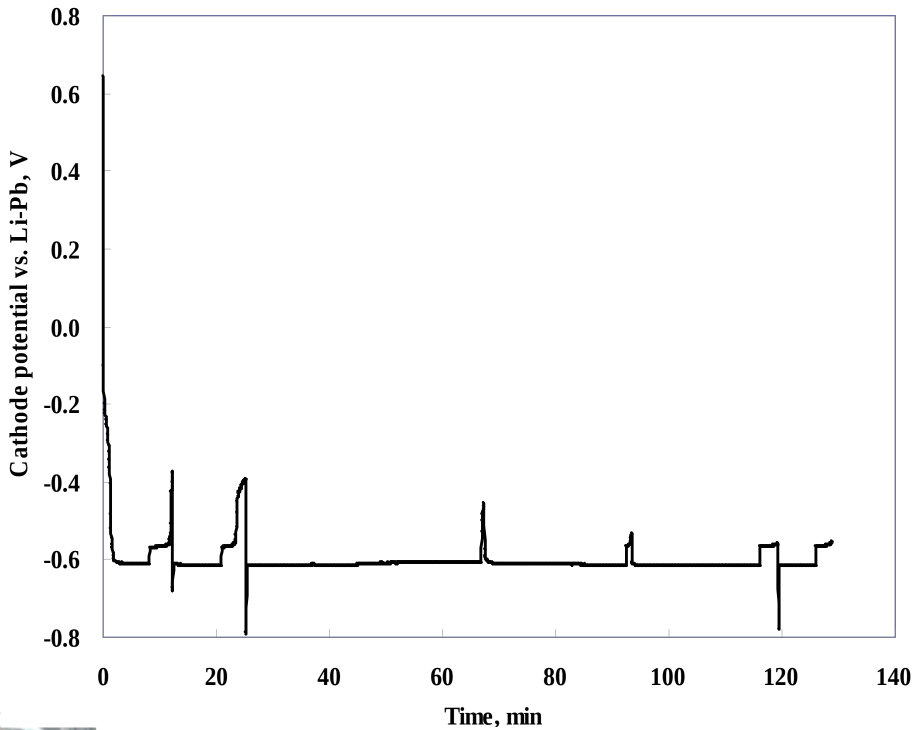
Exchange current: dependent of the anode reaction!!

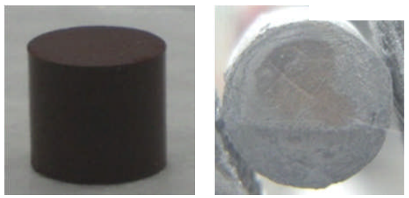
Ratio of Cathode & Anode Surface Area



Electrolytic Reduction of UO_2 w/ BDD anode

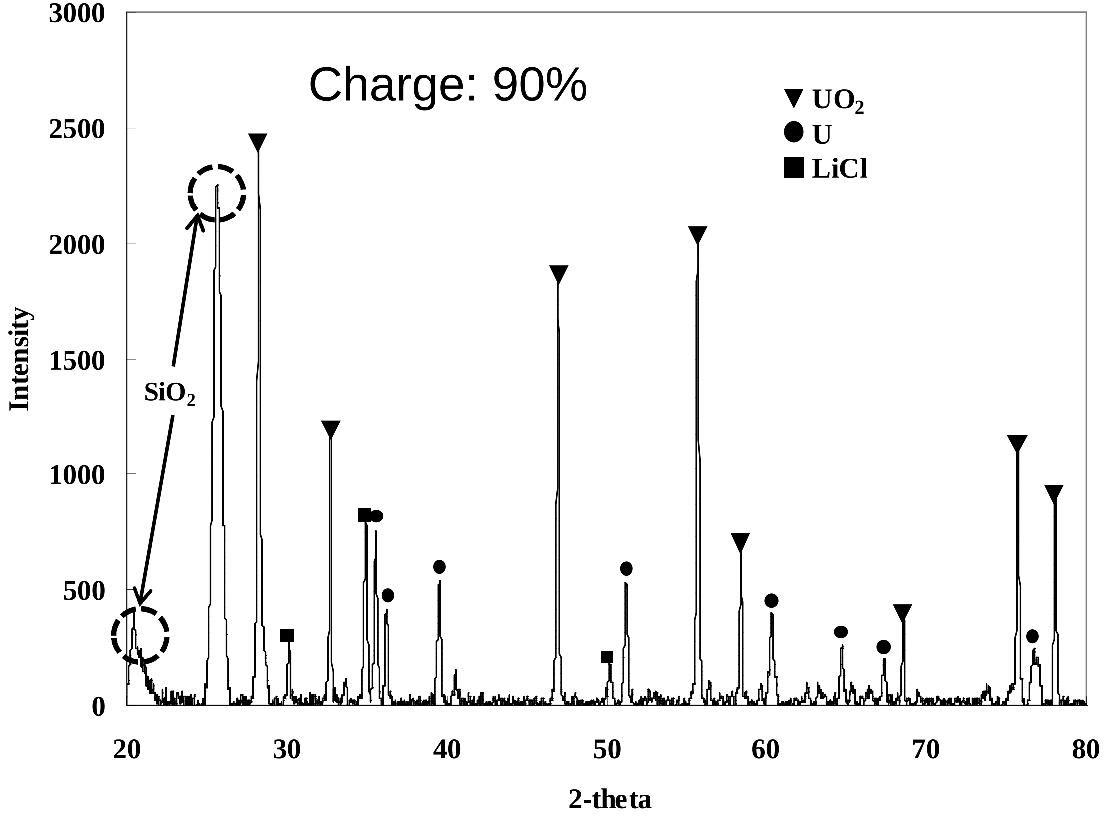






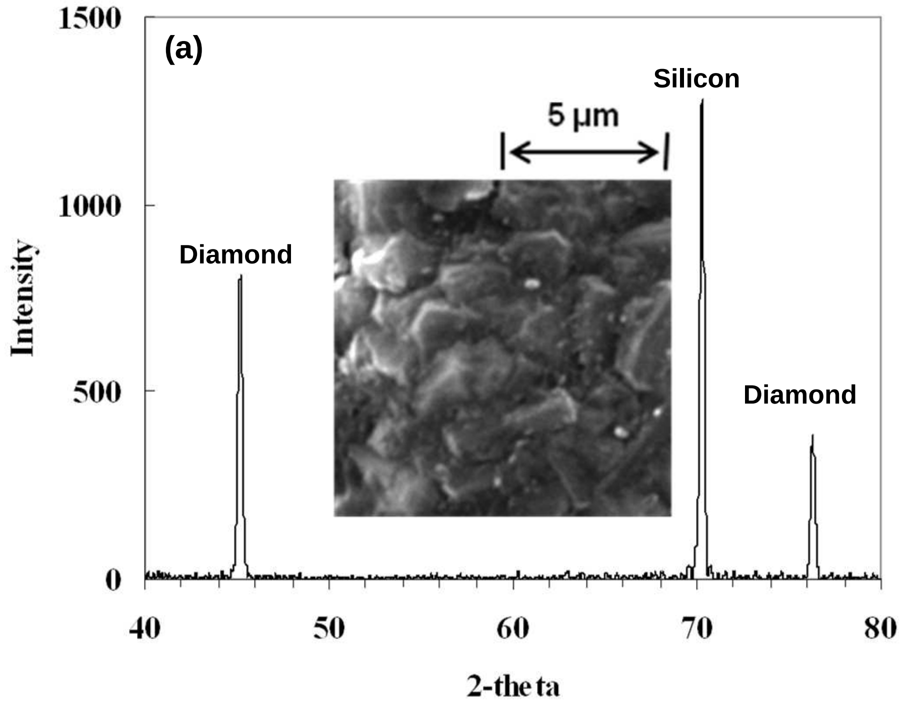
Charge: 0% 90%

Reduced Pellet

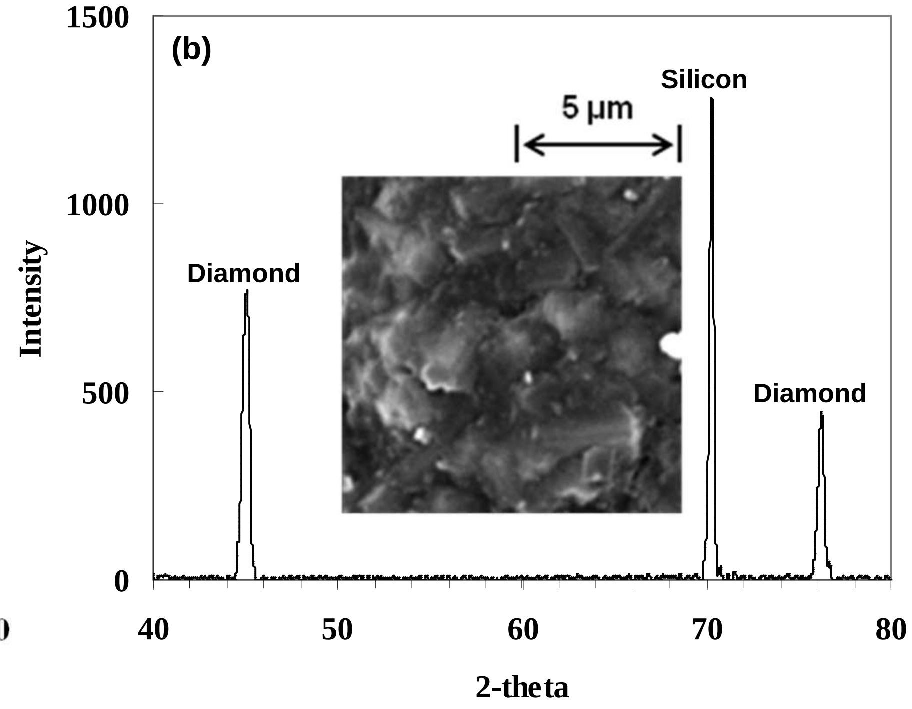


SiO_2 : taping material

BDD Film before/after Reduction Experiment



Before



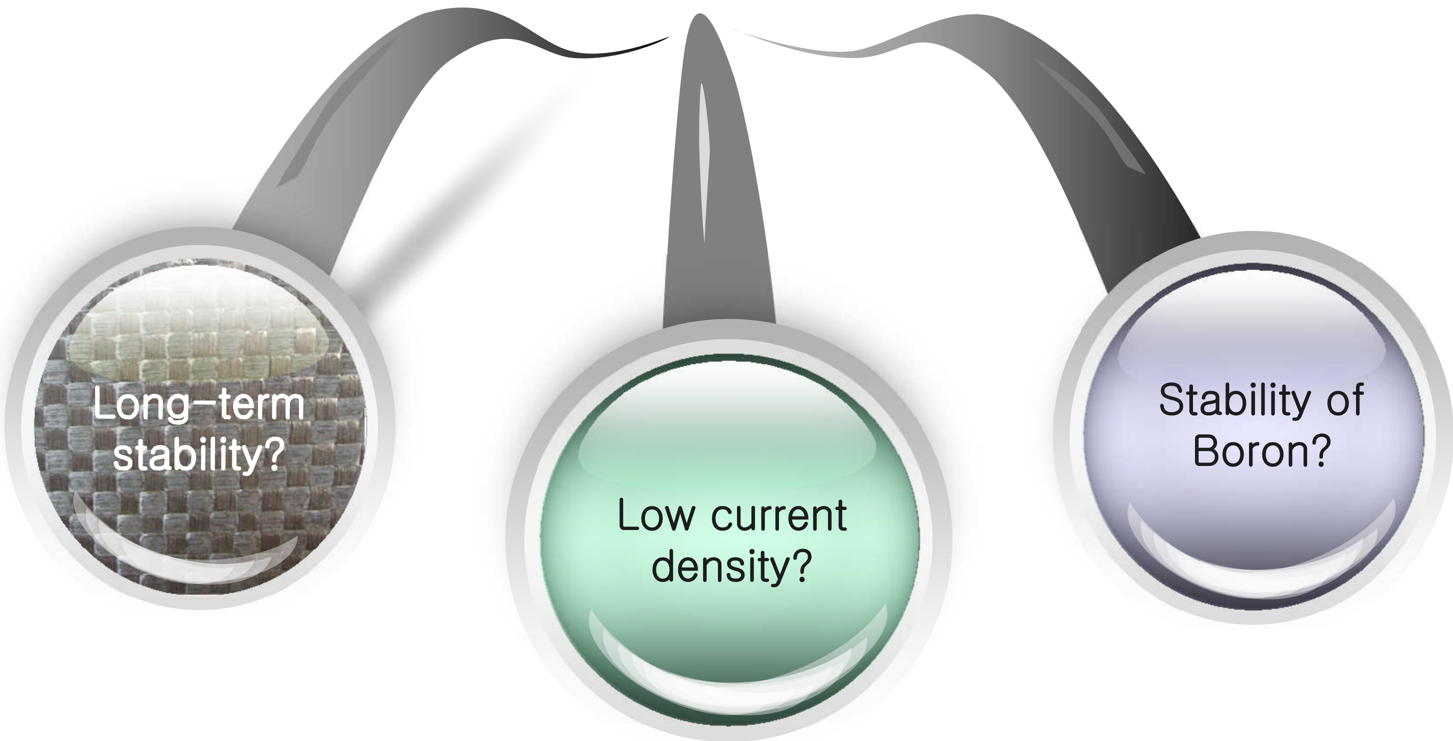
After

IV Conclusions

BDD = an Inert Anode

- BDD as an inert anode (but..short-term operation)
- C/A ratio < 0.63 recommended for UO_2 reduction
- Current density: 34 mA/cm^2

However,



Is Boron permanently stable in Li_2O-LiCl-KCl?

Burning at 550°C?

	Boron	Diamond
$T_{ignition}$, °C	580	720~800 (O_2) 850~1000 (Air)

- Oxygen evolution at 550°C
- Boron will not burn

Oxidation of B to B_2O_3 chemically or electrochemically?

	Melting temperature	$T_{operation}$ = 550°C
B_2O_3	450°C (trigonal) 510°C (tetrahedral)	melting

- Must be proved for a long-term application

Thank you!
Questions?

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