DEVELOPMENT OF ANODE STRUCTURE FOR ELECTROWINNING PROCESS

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Introduction

- To recover group actinides from salt mixture in the electrorefiner
- To produce a U-TRU metal ingot for SFR fuel fabrication
- To minimize high-level waste salt

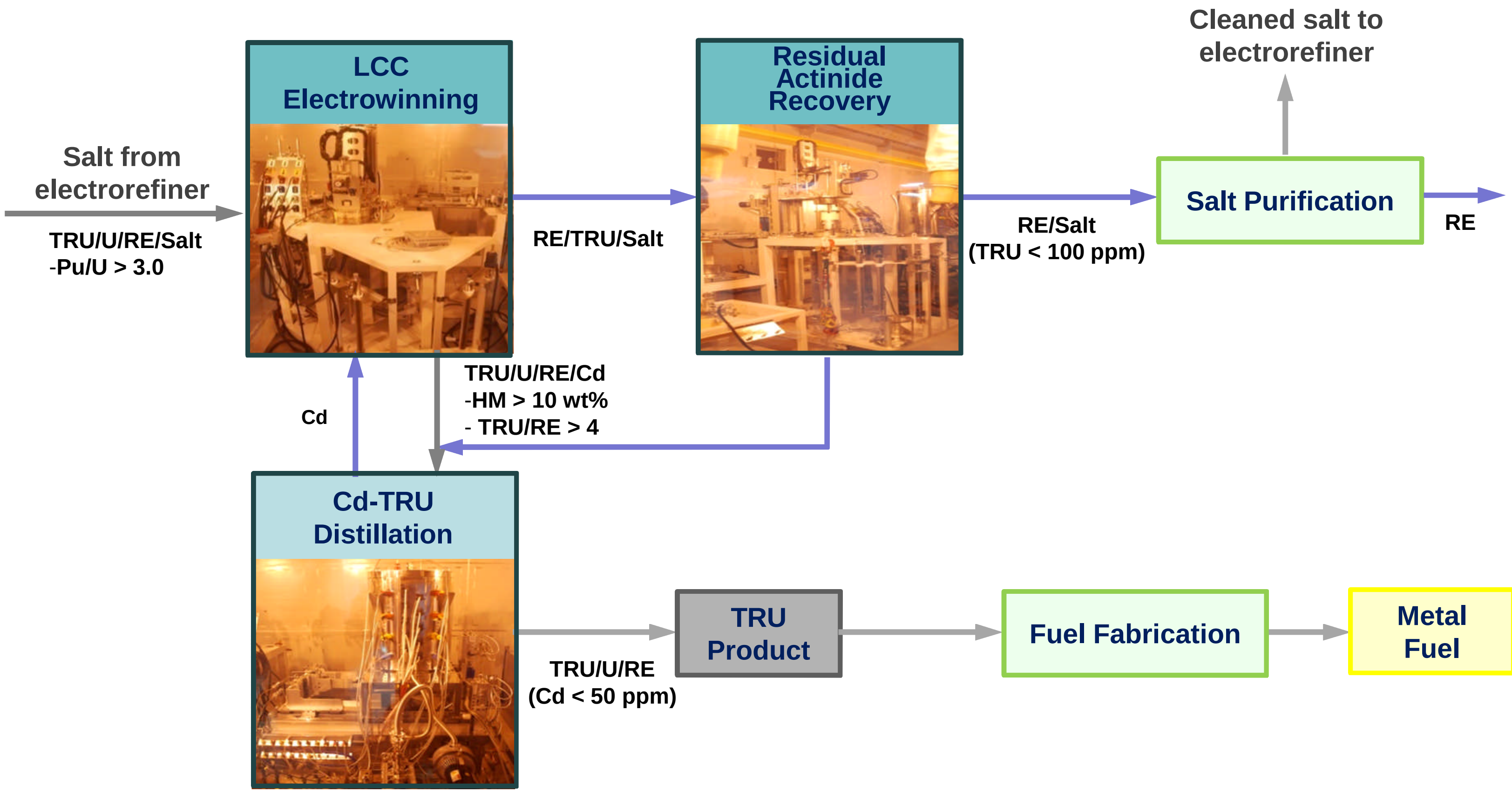
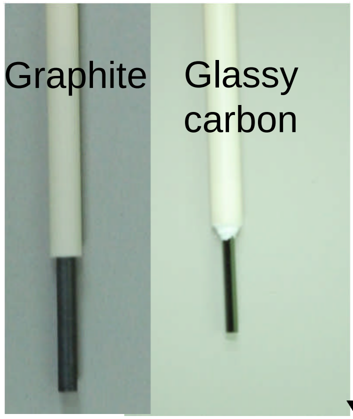


Fig 1. Overview of electrowinning process at KAERI.

LCC Electrowinning @ KAERI



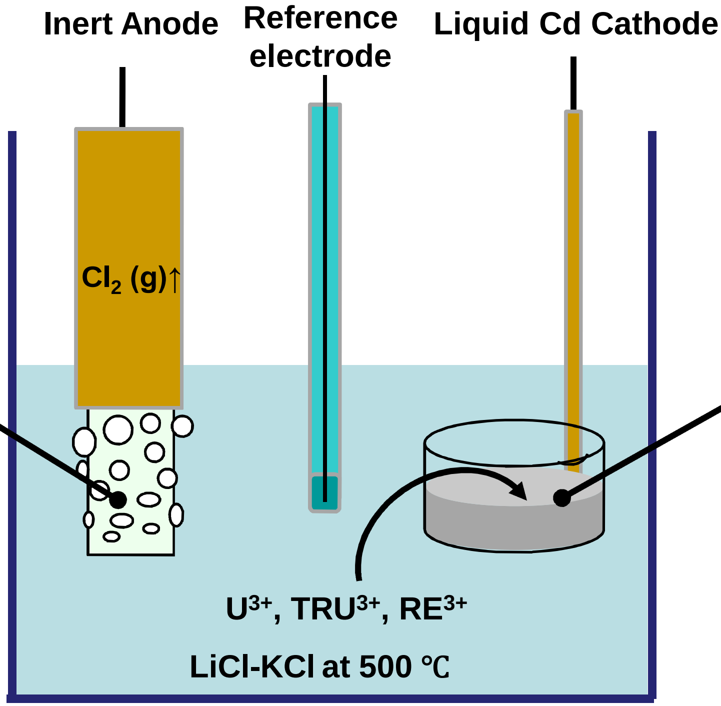
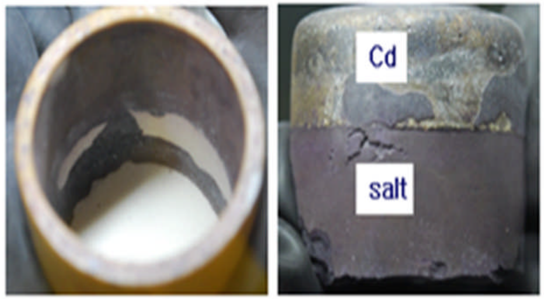


Fig 2. LCC electrowinning cell.



- **Anode : Oxidation**

  $2Cl^- \rightarrow Cl_2 + 2e^-$

- **Cathode : Reduction**

  $U^{3+} + 3e^- \rightarrow U$

  $TRU^{3+} + 3e^- \rightarrow TRU$

  $RE^{3+} + 3e^- \rightarrow RE$

Shroud materials

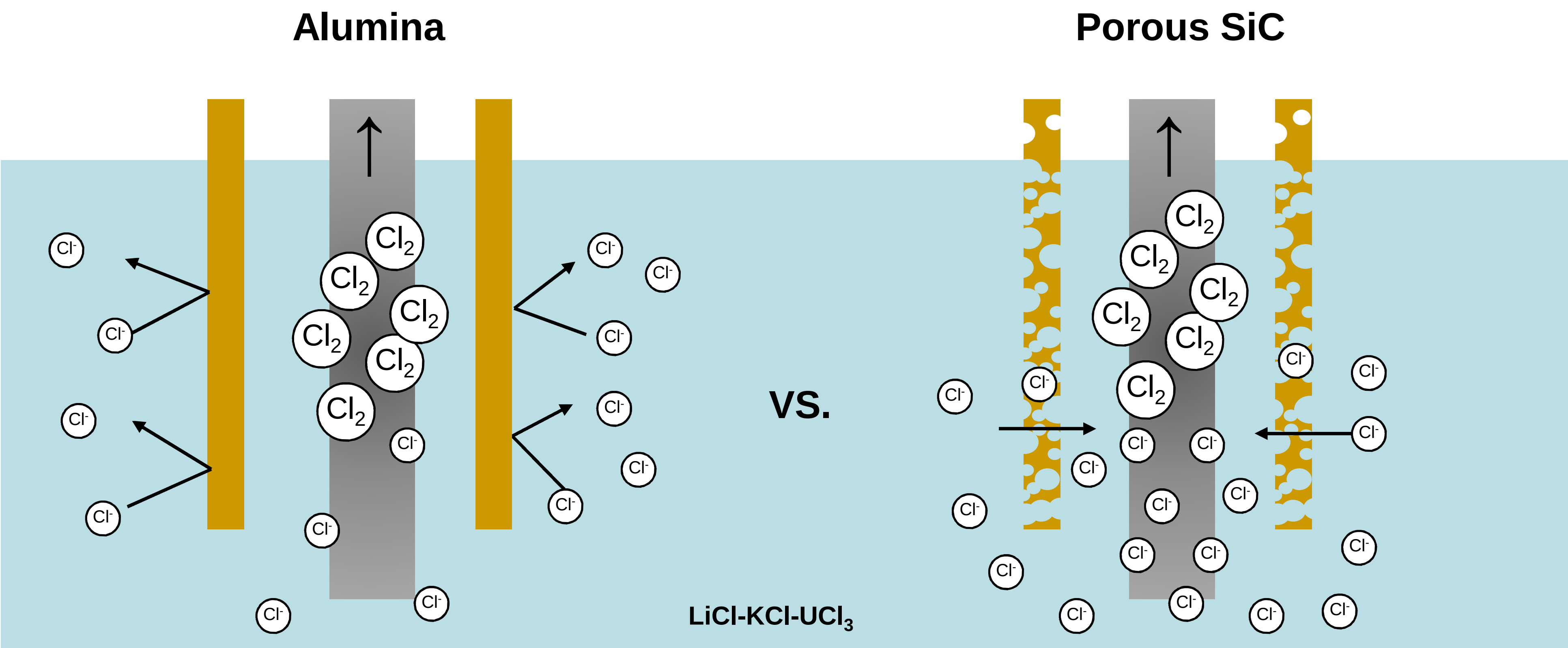


Fig 3. Comparison of shroud materials, alumina vs. porous SiC, for Cl_2 producing anode.

Reactivity with UCl_3

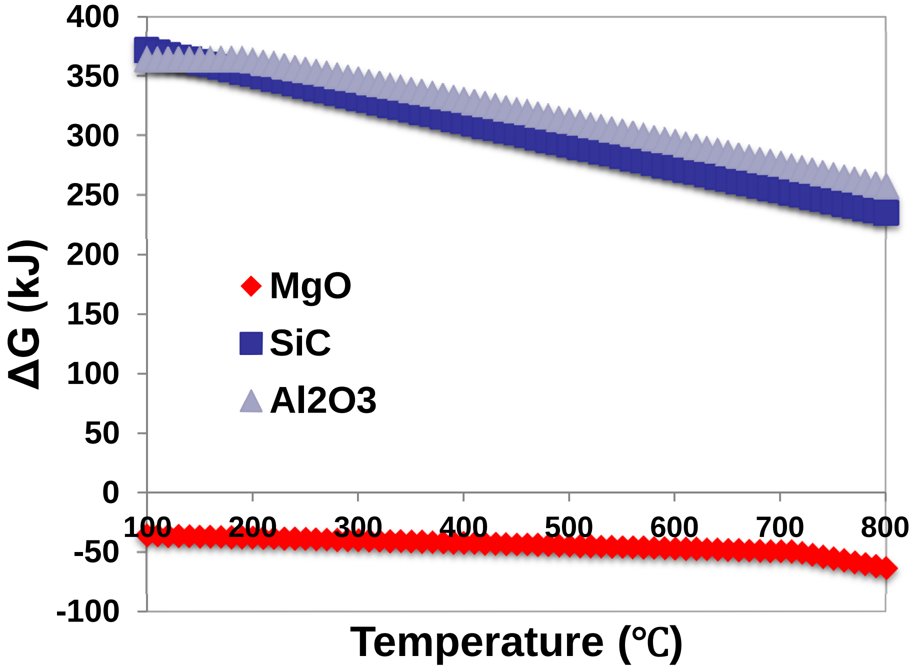
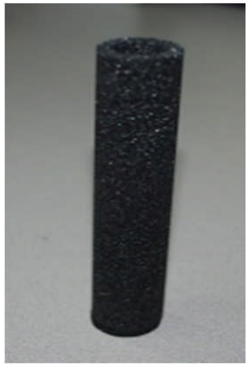


Fig 4. Calculation of ΔG for the reaction of various shroud materials with UCl_3 at temperature in the range of 100 – 800 ℃.

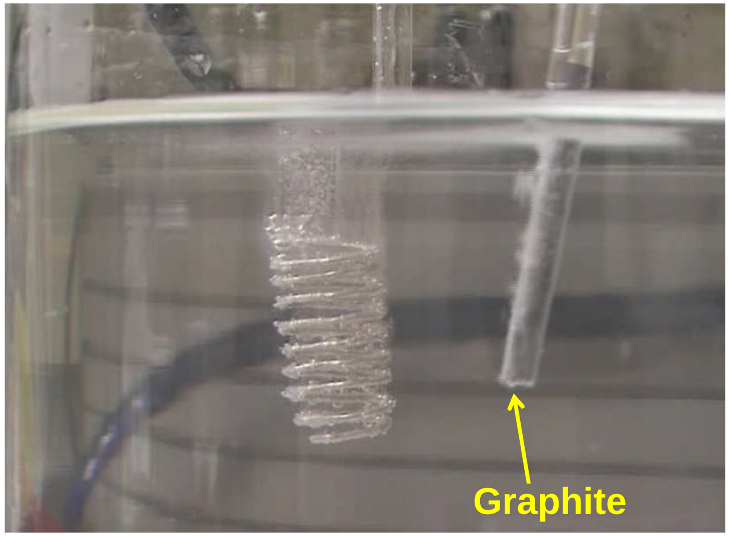
MgO
Porous structure
Reactive to UCl_3
$MgO + UCl_3 = MgCl_2 + UO + UO_2$



SiC
Porous structure
No reactivity

Al_2O_3
Non-porous structure
No reactivity

Preliminary study (1)



VS.

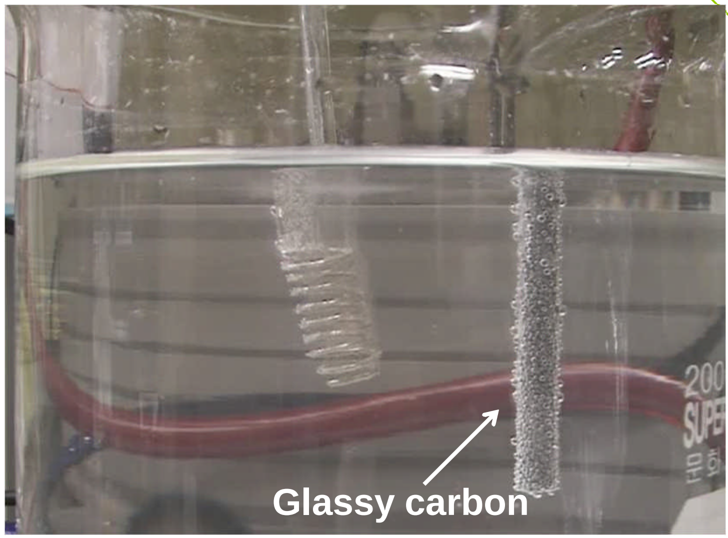


Fig 5. Comparison of gas evolution on the inert carbon materials, graphite (left) and glassy carbon (right).

Graphite

Gas bubbles are detached from the electrode surface and disappear as soon as they are generated.

No significant effect on the electrode surface area.

Glassy carbon

Gas bubbles occupy the electrode surface until their sizes grow big enough to detach.

Decrease in the electrode surface area.

Preliminary study (2)

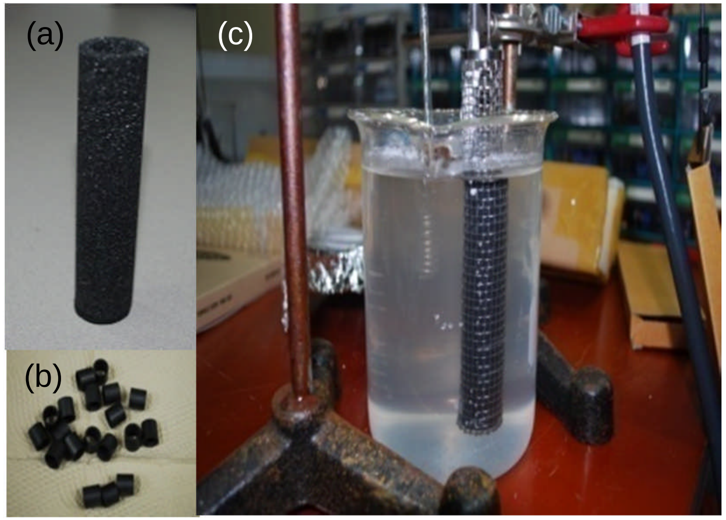


Fig 6. Picture of (a) SiC tube, (b) graphite tubes, (c) electrochemical cell. WE: graphite tubes with SiC shroud, CE: Pt wire, RE: Ag/AgCl (sat'd KCl), Electrolyte: 1.7 M Na_2SO_4.

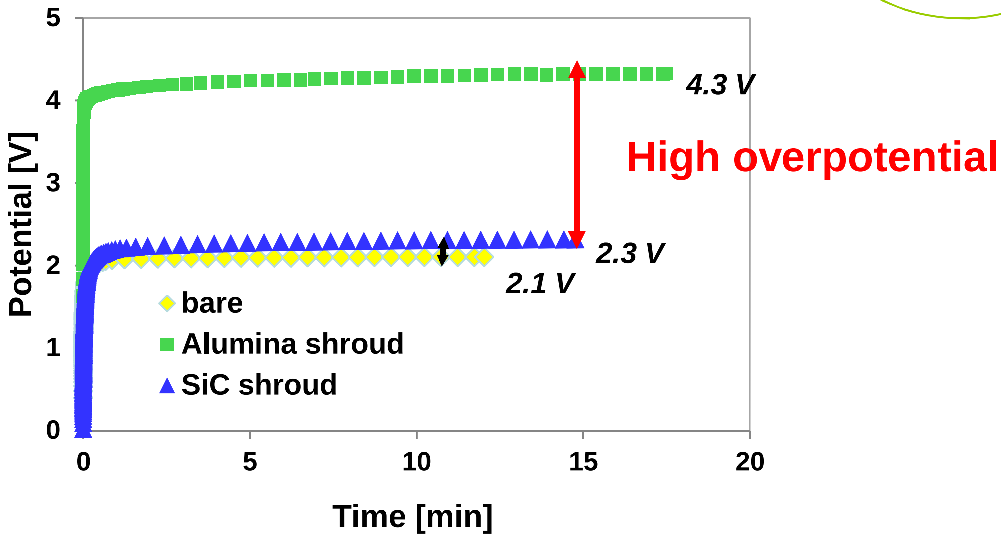
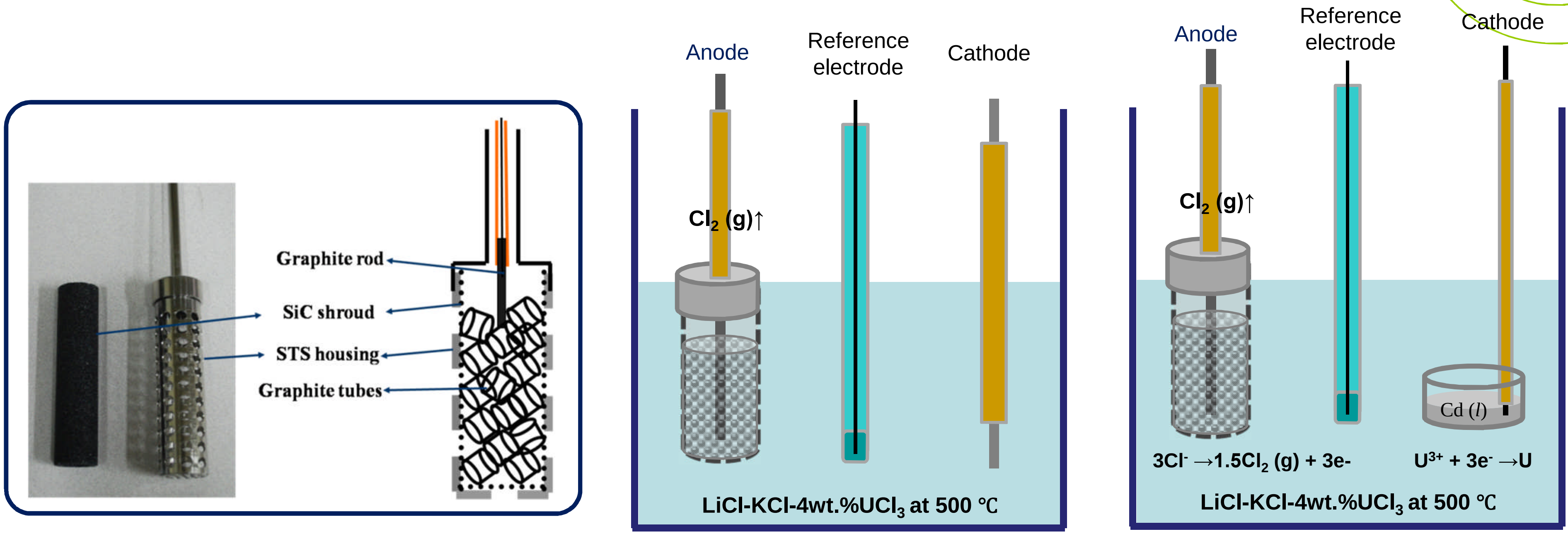


Fig 7. Comparison of the anode potential under the water electrolysis at 200 mA.

- During the electrolysis, the potential of anode using SiC shroud was 2.3 V vs. Ag/AgCl, which is close to that of the bare one.
- When an alumina tube was used as a shroud, the anode potential was 4.3 V vs. Ag/AgCl much higher than that of SiC shroud.
- SiC tube has porous structure which helps the movement of ions to the electrode surface, resulting in no significant overpotential.

Experimental setup

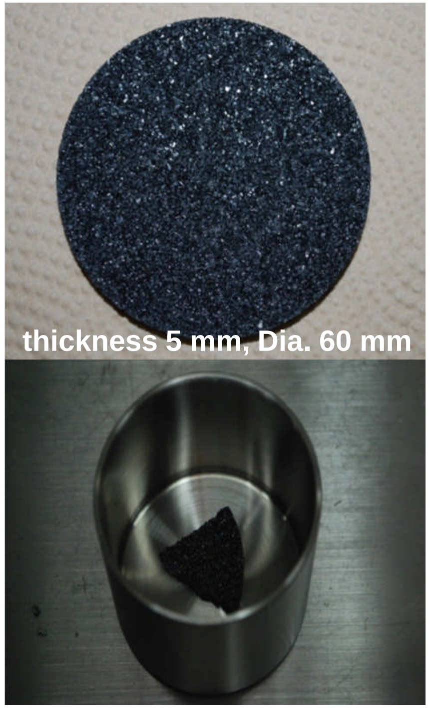


(a) Anode structure *(b) For voltammetry, EIS* *(c) For deposition test*

Fig 8. Picture of the anode structure used in this study (a) and schematic diagrams of the electrochemical cell (b-c).

- Alumina crucible (ID 70 mm) for salt (LiCl-KCl-4 wt. % UCl_3) container
- Cathode: Mo rod (Φ 3 mm) or Cd (20 g) in Pyrex crucible (ID 15 mm) with a lead wire (Mo)
- Reference electrode: Ag wire (dia. = 1 mm) in 1 mol% AgCl-LiCl-KCl
- Anode: graphite rod (Φ 3 mm)/ tubes (OD 10 mm, ID 8 mm, H 10 mm)
  with a SiC tube (bottom blocked, OD 20 mm, ID 15 mm, H 100 mm, porosity 30 %, purity 98.5 – 98.8 %)
- O_2 & H_2O < 10 ppm, Temperature 773 K
- Bio-Logic SP-300 (potentiostat/galvanostat) with VMP3

Stability of SiC @ 500 ℃



For 1 week at 500 ℃

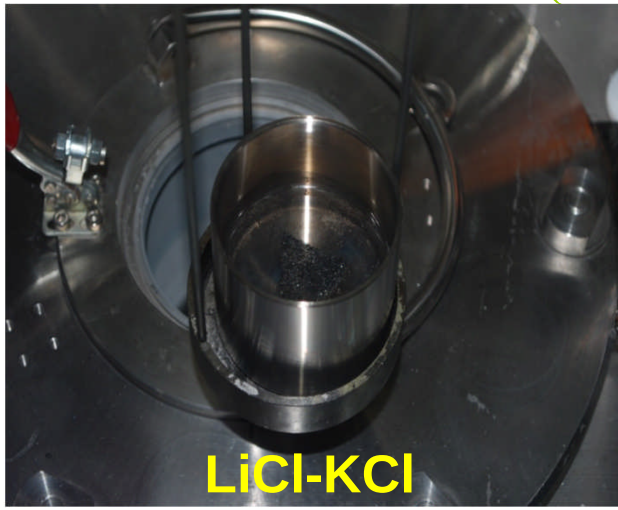
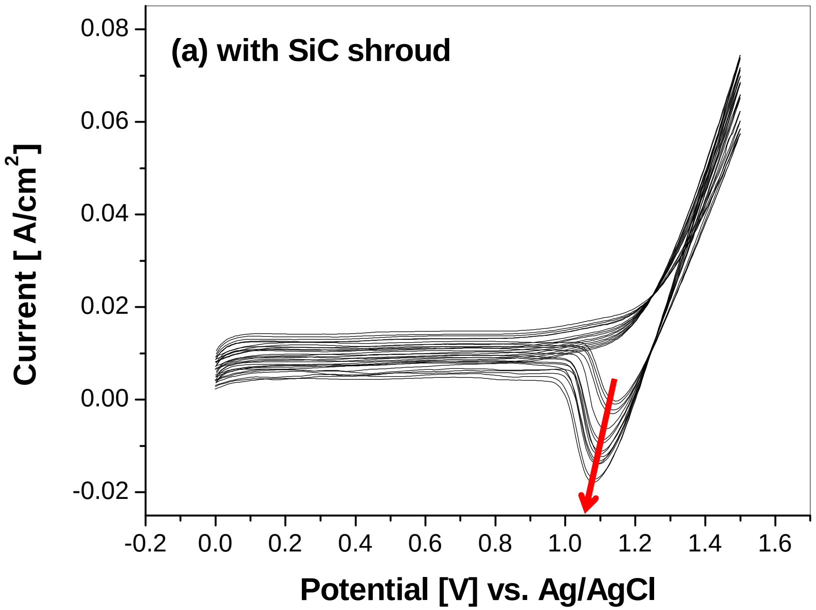


Fig 9. Stability test of SiC in LiCl-KCl and 4 wt% UCl_3-LiCl-KCl at 500 ℃.

Cyclic Voltammetry



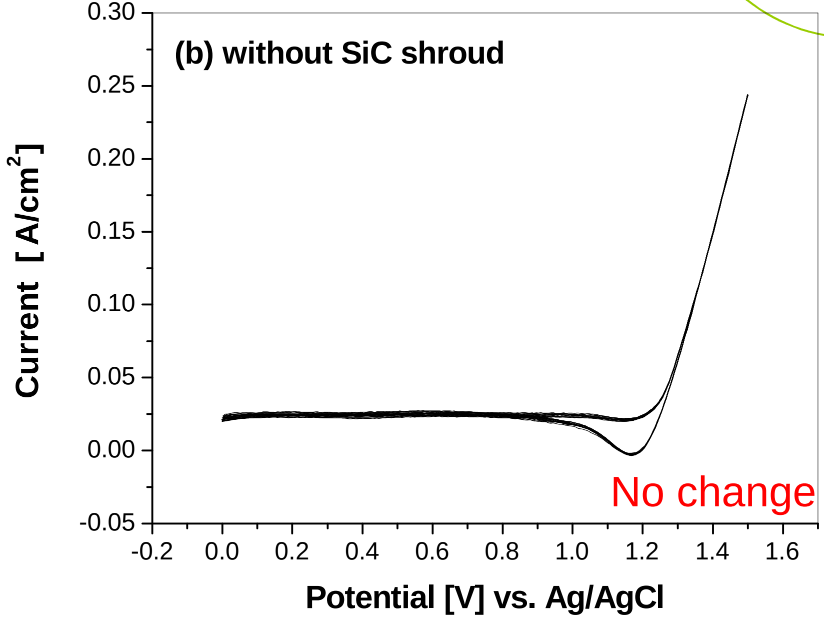


Fig 10. Cyclic voltammogram of graphite anode (a) with and (b) without a SiC shroud in LiCl-KCl-4 wt% UCl_3 (scan rate = 100 mV/s, number of repeated scanning = 16 times).

- CV was carried out in LiCl-KCl-4 wt% UCl_3 at 773 K to investigate the effect of a SiC tube on the anodic behavior of a graphite rod.
- The redox potential of Cl^-/Cl_2 was about 1.3 V vs. Ag/AgCl regardless of the use of the SiC shroud.
- About four times lower current density was found when a SiC shroud was used.
- More interestingly, the reduction peak current (I_{pc}) indicated that the $Cl_2 + 2e \rightarrow 2Cl^-$ increased when the SiC tube was applied, while no changes in the cyclic voltammograms were found when no shroud was used.

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Cl_2 capture indicated by increase of I_{pc}

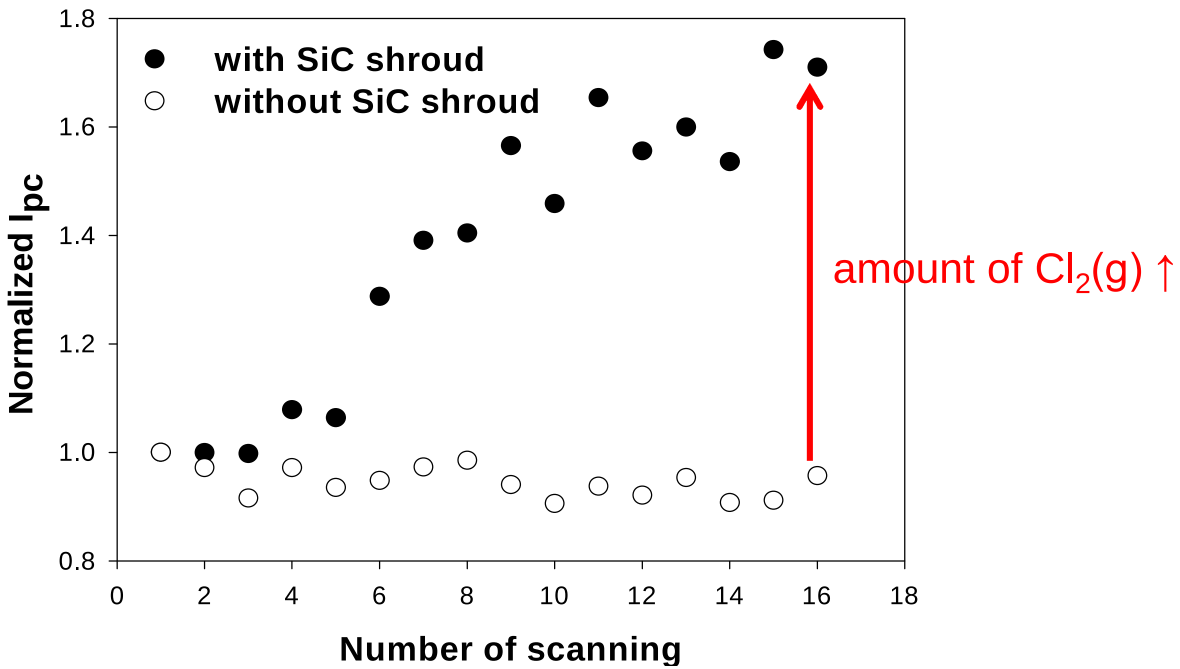


Fig 11. The change of normalized I_{pc} depending on the sweep numbers from Fig. 9.

- The I_{pc} at the shrouded anode increased about 70 % after 16 repeated scans, but no changes in bare anode.
- This may be due to some of the Cl_2 (g) being captured inside the SiC shroud during the repeated scans. Since the density of Cl_2 (g) is larger than that of Ar (g) in a globe box, some of the Cl_2 (g) can occupy inside the SiC shroud, which indicates that a selective separation can be achieved with the help of an exterior venting system.

Potential-current relation

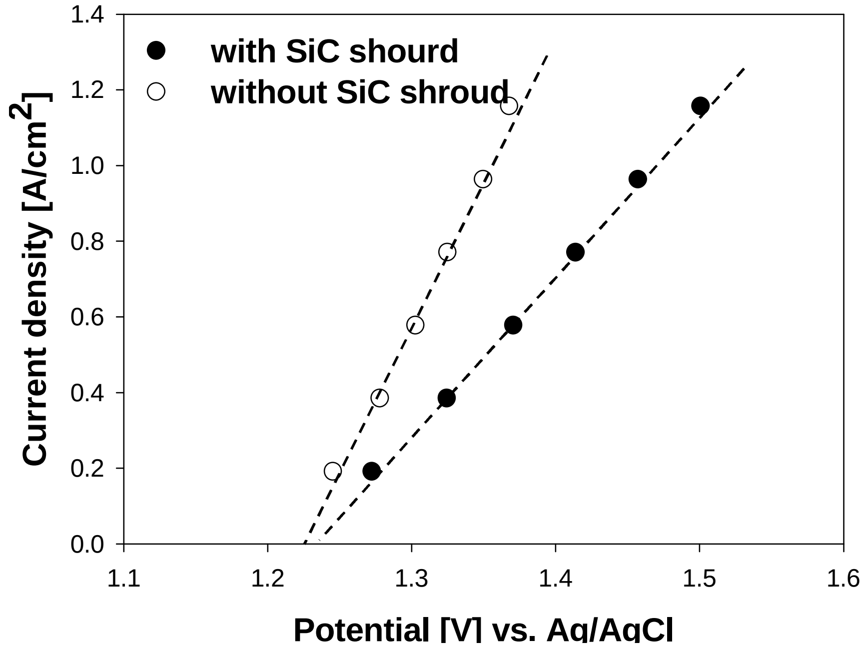


Fig 12. Anodic polarization curves of graphite anode (a) with and (b) without a SiC shroud in LiCl-KCl-4 wt% UCl_3.

- No significant potential difference when the applied current density was low.
- At 0.2 A/cm^2, the potential difference was about 27 mV.
- Less effect of SiC shroud on the anode overpotential

Impedance measurement

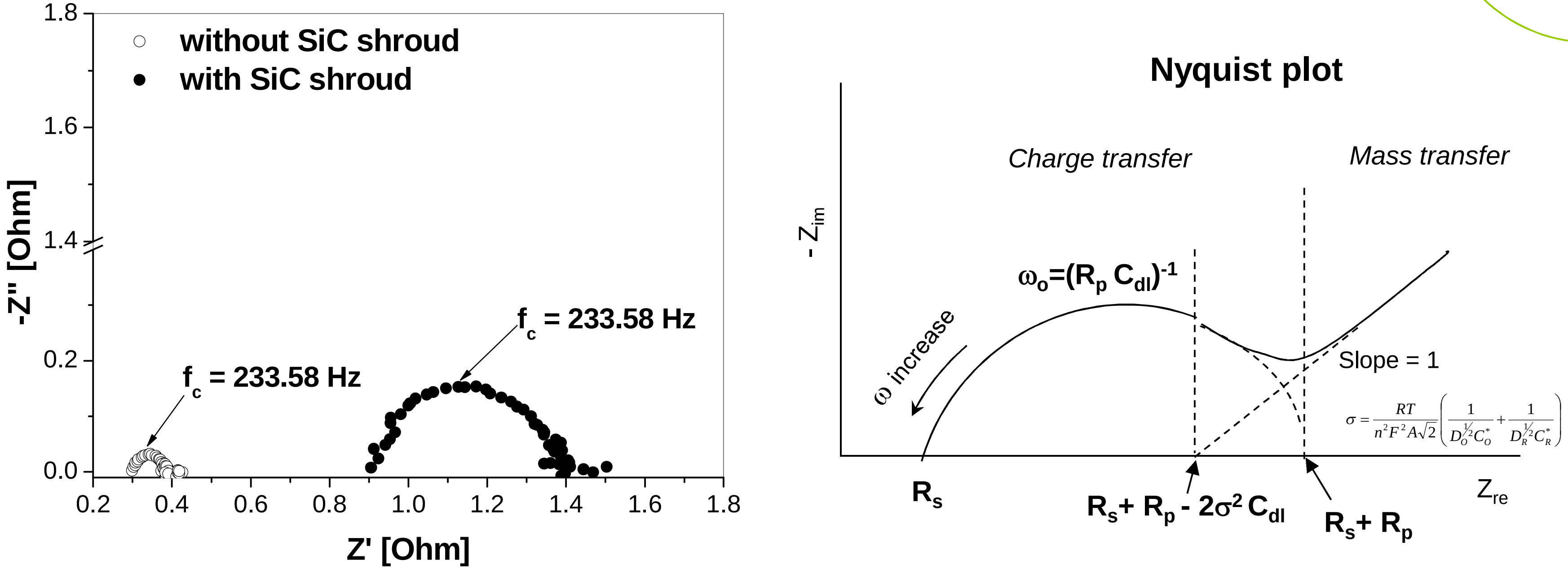


Fig 13. The effect of SiC shroud on the impedance response in LiCl-KCl-4 wt% UCl_3 at 1.3 V vs. Ag/AgCl at 773 K.

- A semi-circle in the high frequency range, followed by a linear behavior
- In case of braphite rod, the salt resistance (R_s) and the charge transfer resistance (R_p) were determined to be 0.3 and 0.04 Ω, respectively.
- When a SiC shroud was applied, the R_s and R_p increased to 0.9 and 0.24 Ω, respectively.
- The double-layer capacitance (C_{dl}) increased from 2.8 μF to 17 μF by the application of a SiC shroud due to its porous structure.

Effect of surface area

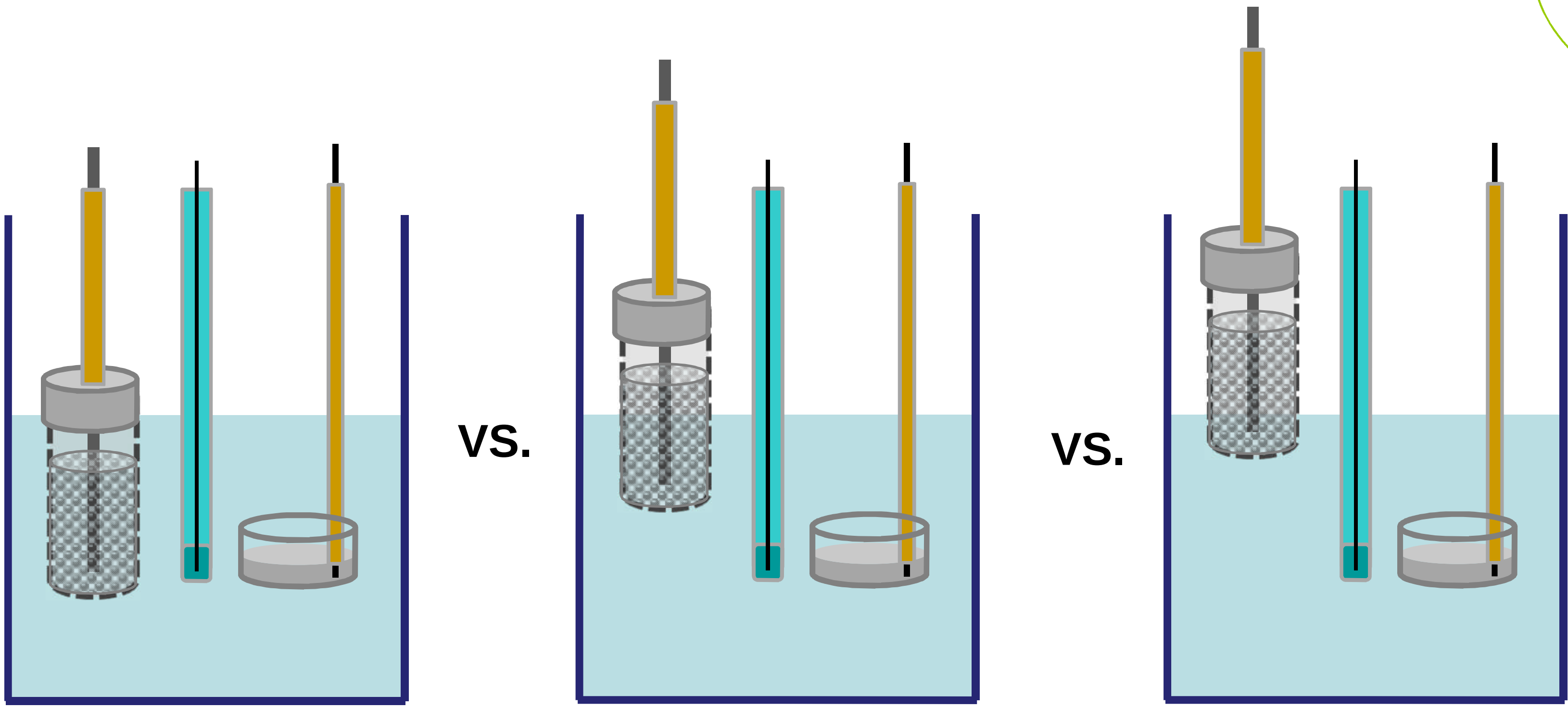


Fig 14. Effect of surface area ratio of anode/cathode by varying the dipping height of anode.

- The effect of surface ratio (anode/cathode) on the anode potential was examined by varying the dipping height of the anode (graphite rod with SiC) in LiCl-KCl-4 wt% UCl_3.
- The surface area of cathode was kept at 1.766 cm^2.
- The anode potential was monitored for 30 min during the electrodeposition of U at 100 mA/cm^2
- Note that the presented anode surface area is the geometric area not the real one which is considering the roughness of the electrode surface.

Effect of surface area (cont'd)

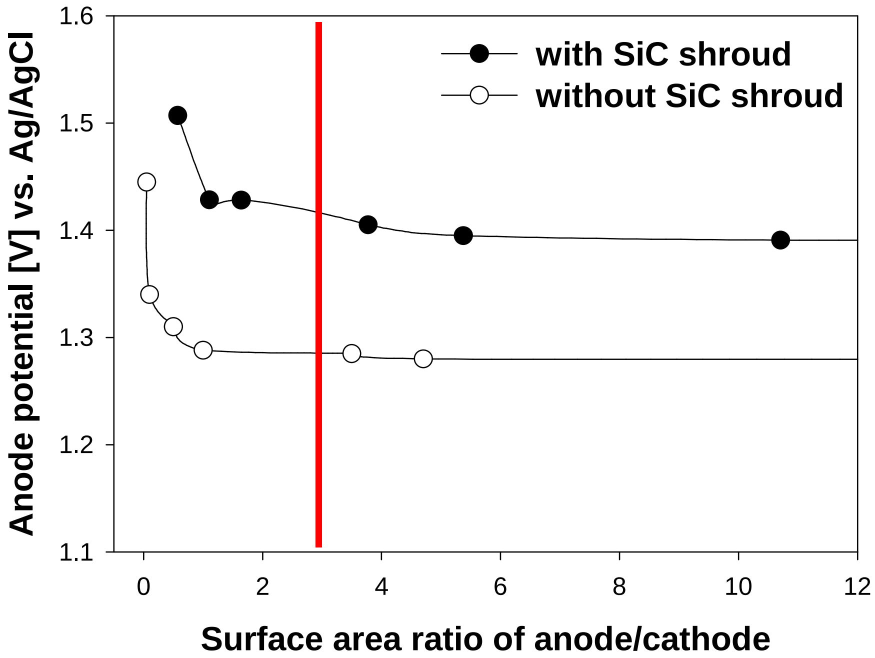
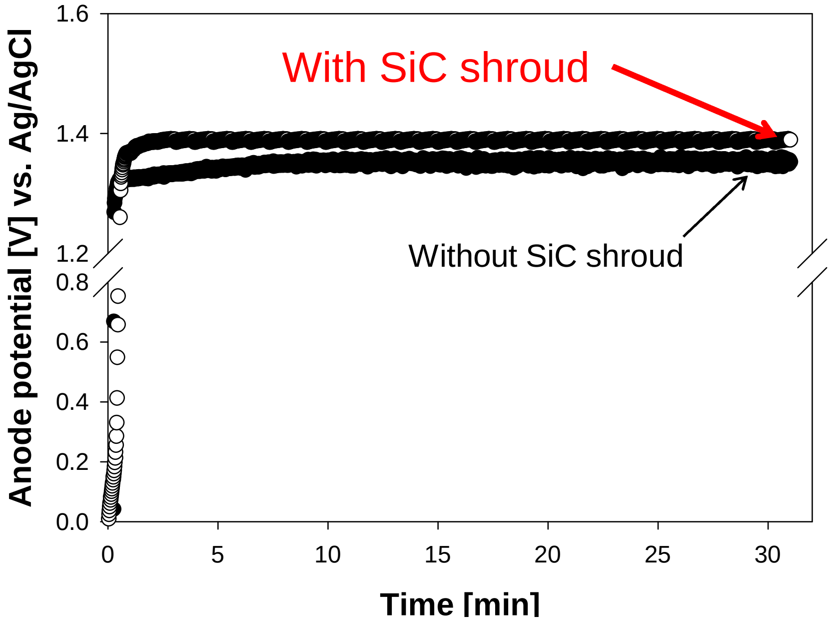


Fig 15. Effect of anode surface area on the anode potential during the electrodeposition of U^{3+} at 100 mA/cm^2.

- The anode potential decreased initially and then reached a plateau (i.e., 1.39 V) as the surface area of anode increased. That means, higher overpotential was loaded when no enough surface area of anode was provided.
- For comparison, the anode potential was 1.28 V when no SiC shroud was applied.
- The optimum surface ratio of anode/cathode for the electrowinning process was determined to be 3: 1

Performance evaluation during electrowinning



- ✓ Evaluation of the anode by observing the anode potential during the electrowinning process
- ✓ U deposition onto a Cd in LiCl-KCl-4 wt% UCl_3 at 100 mA/cm^2 for 30 min
- ✓ Total amount of charge passed = 318 C
  ~ saturation of Cd (20 g) with U
- ✓ Note that the cathode potentials were -1.71 ~ -1.75 V

Fig 16. Effect of SiC shroud on the anode potential profiles during the galvanostatic electrolysis in LiCl-KCl-4 wt% UCl_3.

- The potential of graphite tubes with a SiC shroud was kept at around 1.39 V vs. Ag/AgCl during the galvanostatic electrolysis accompanied with chlorine evolution.
- For comparison, the anodic potential of graphite tubes was 1.35 V vs. Ag/AgCl.
- The use of SiC shroud did not significantly affect the anode potential during the U recovery, showing a negligible loading of overpotential.
- Also, the SiC shroud was stable with the chlorine evolution (result not shown).
- The anode structure is adjustable in an electrolytic U recovery system in a LiCl-KCl eutectic melt.

Summary

- An anode structure using a SiC shroud and graphite tubes for electrowinning process was demonstrated.
- The porous structure of SiC allows more efficient contact of electrode surface to LiCl-KCl eutectic melt.
- The feasibility of Cl_2 (g) capture by the employment of SiC was evaluated from the increase of I_{pc} in repeated CV scans.
- The use of inert graphite tubes enables to provide enough surface area, resulting in no significant anodic overpotential.
- During the U deposition test, the potential of shrouded anode was very stable and a negligible overpotential was observed.
- For further research, a quantitative analysis will be performed by GC with the modification of experimental setup. (-ing)
- The anode structure in this work will be applied in the engineering-scale electrowinning cell.

Thank you for listening!

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