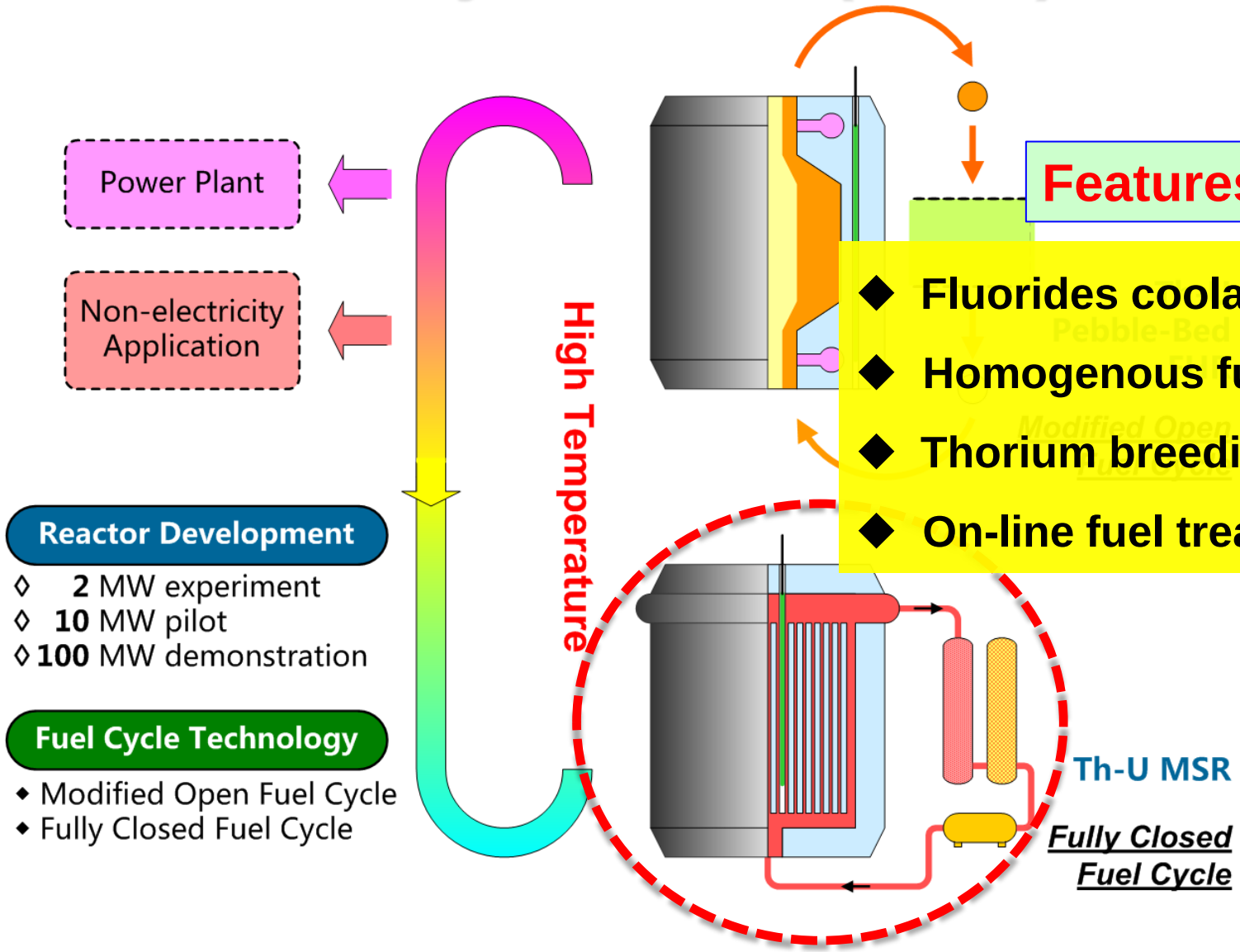
Electrochemical behaviors of U, Th in fluoride molten salts

Dewu Long, Wei Huang, Qingnuan Li

Shanghai Institute of Applied Physics (SINAP), Chinese Academy of Sciences(CAS)

INTERNATIONAL PYROPROCESSING RESEARCH CONFERENCE 2014
IDAHO FALLS, IDAHO, OCT. 19-23, 2014

TMSR Project at SINAP (CHINA)

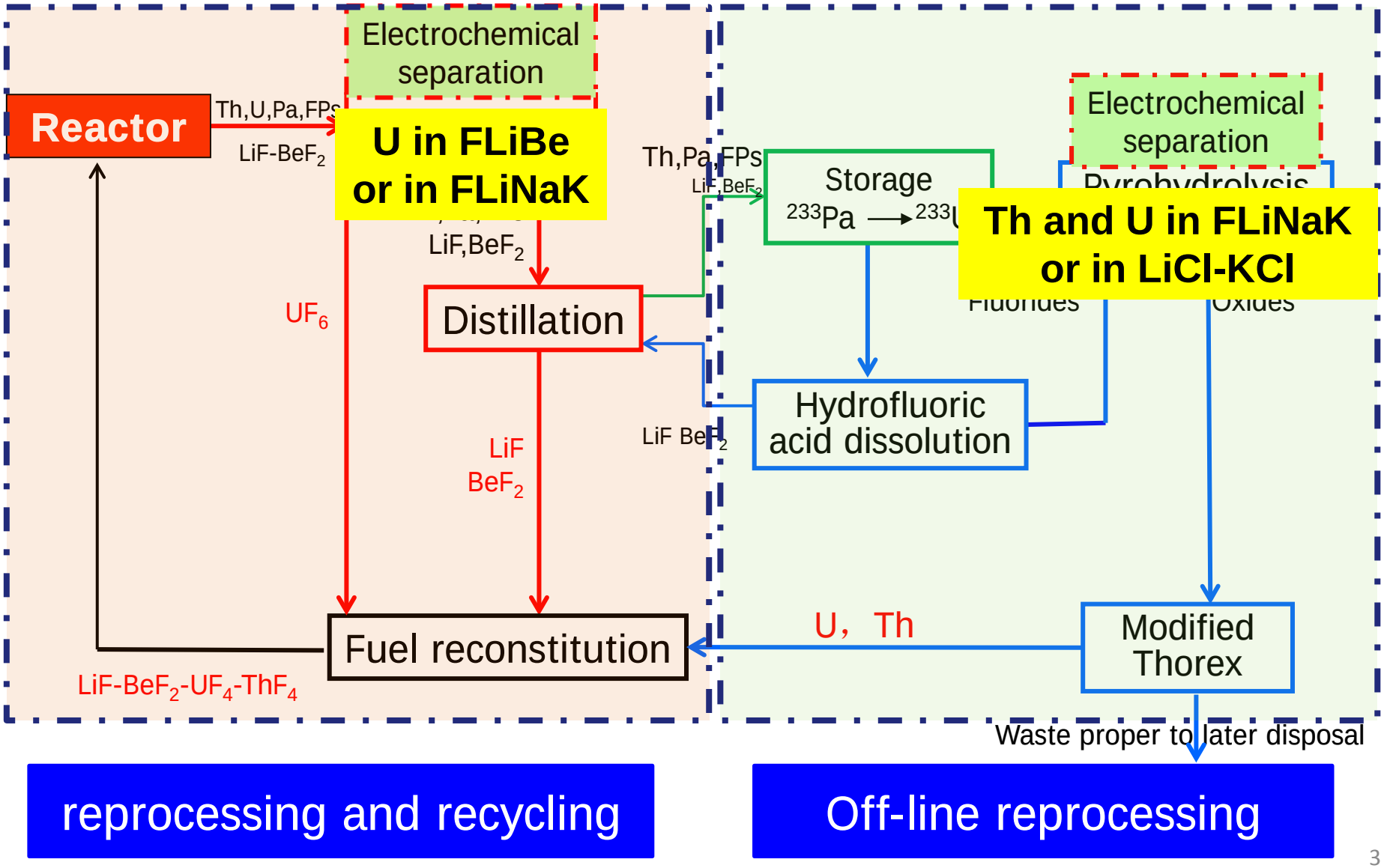


Features

- ◆ Fluorides coolant
- ◆ Homogenous fuel
- ◆ Thorium breeding
- ◆ On-line fuel treatment

Scheme of TMSR Developing Strategy

Conceptual flowsheet of TMSR Fuel Processing



Challenges for the implementation of electrochemical separation technology in TMSR

- **Fluoride-based molten salt medium**. One or more steps of the electrochemical separation in TMSR fuel processing have to be conducted in fluoride electrolyte, e.g. $LiF-BeF_2$.
- **Fundamental database unavailable**. The lack of reliable and systematic database of Ans and Lns in fluoride molten salt.
- **The feasibility for recovering of U or Th and the efficiency of the separation process**. The applicability of electrochemical separation method in TMSR fuel processing and the recovery efficient should be evaluated.

Background

Molten salts used in TMSR

FLiBe (^7LiF-BeF_2 66-34 mol%, *m. p.* 460 ℃)

- ✓ Thermal stability
- ✓ Low vapor pressure
- ✓ Manageable melting point
- ✓ Low neutron cross section
- ✓ Radiation resistance
- ✓ Dissolvable media for Ans and Lns
- ✓ Toxicity and poison
- ✓ High cost for Li-7

Due to the toxicity of LiF-BeF_2, LiF-NaF-KF (46.5- 11.5- 42.0 mol%, FLiNaK, *m. p.* 454℃) is initially adopted as the medium.

The R&D of electrochemical technology in TMSP

- ☐ Fundamental data acquisition
- ☐ Electrochemical measurement method
- ☐ Electrochemical deposition

Fabrication and Performance of Reference Electrode

- performance of reference electrode is essential .
- Non-commercial electrode available.

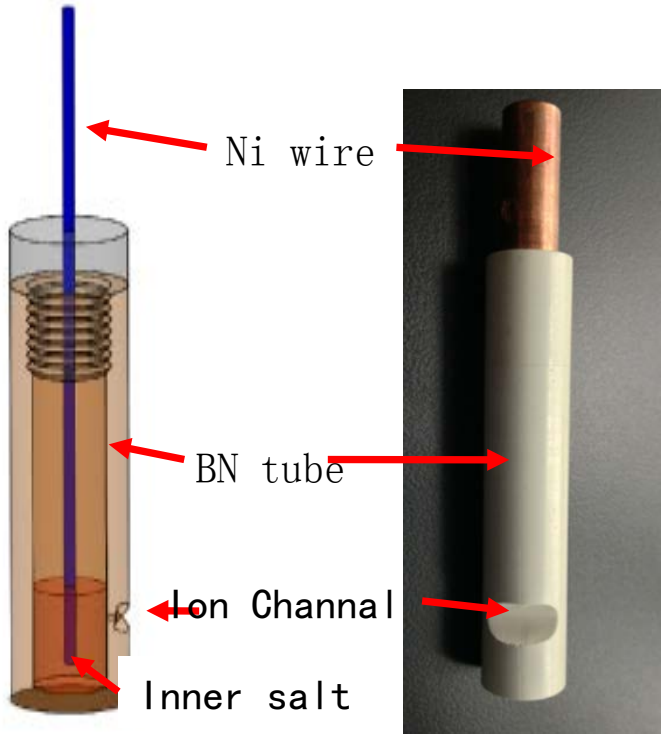
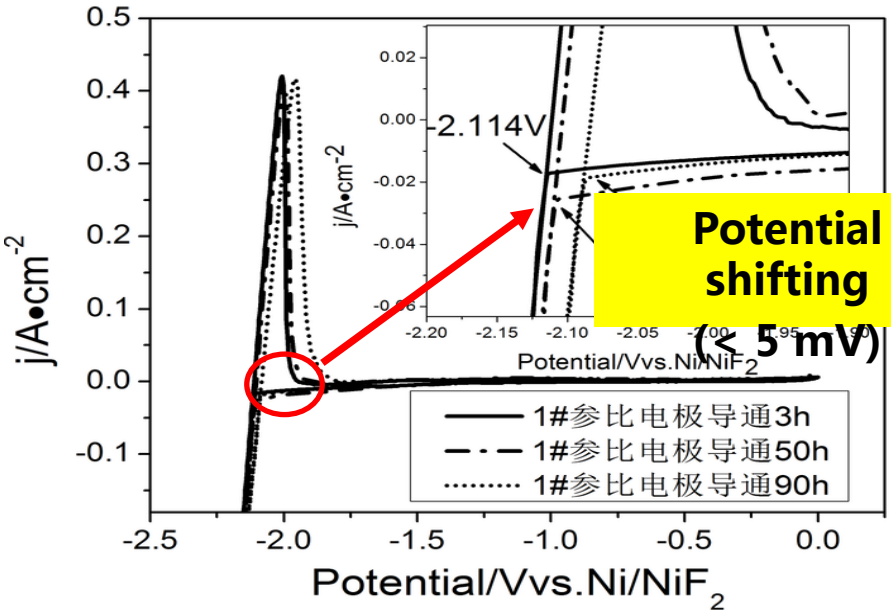


Illustration of reference electrode

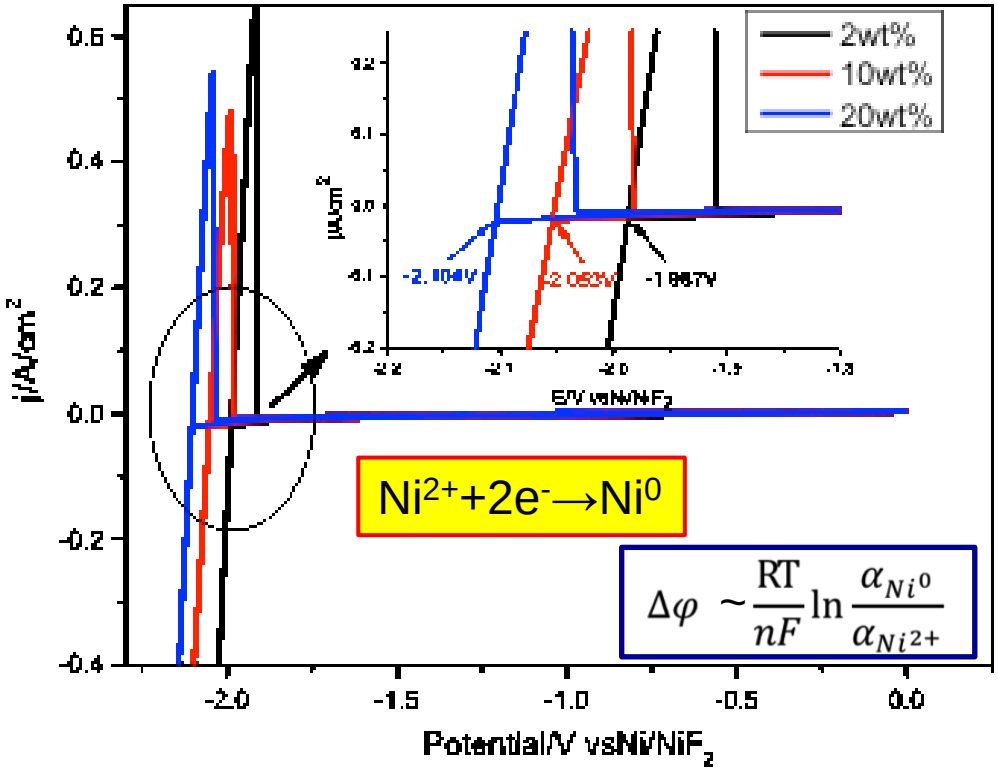


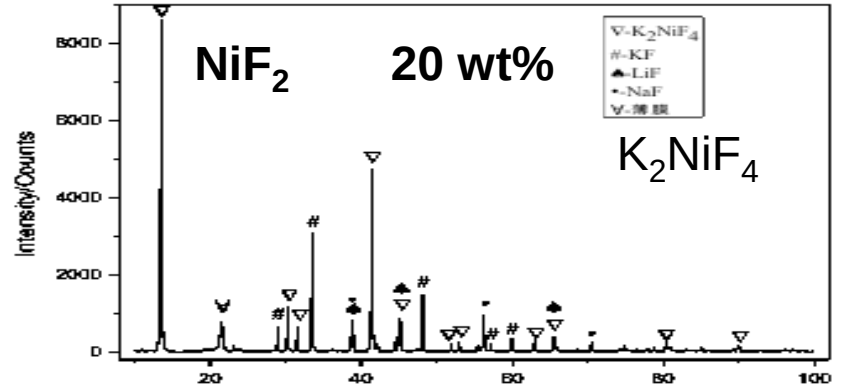
Potential shifting (< 5 mV)

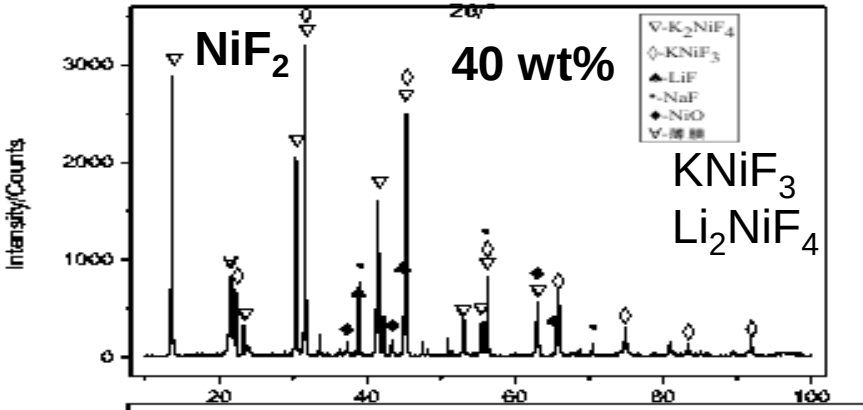
Performance of as-prepared RE

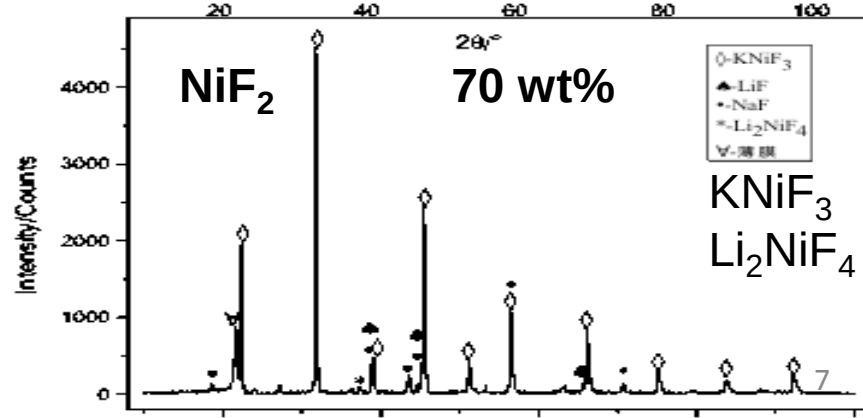
- ✧ Over 50 hrs stability , shifting less than 10mV
- ✧ Excellent repeatability, potential deviation less than 5mV
- ✧ **Suitable for experimental requirement**

On mechanism understanding the performance of an reference Electrode



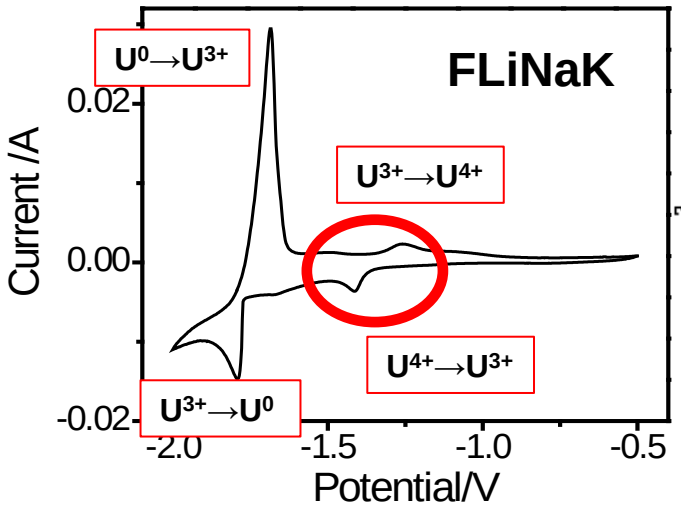


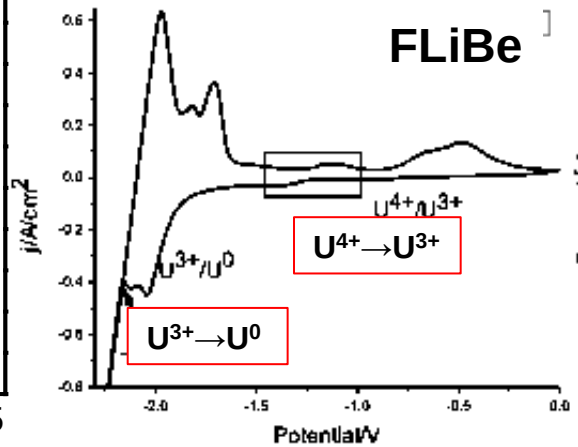


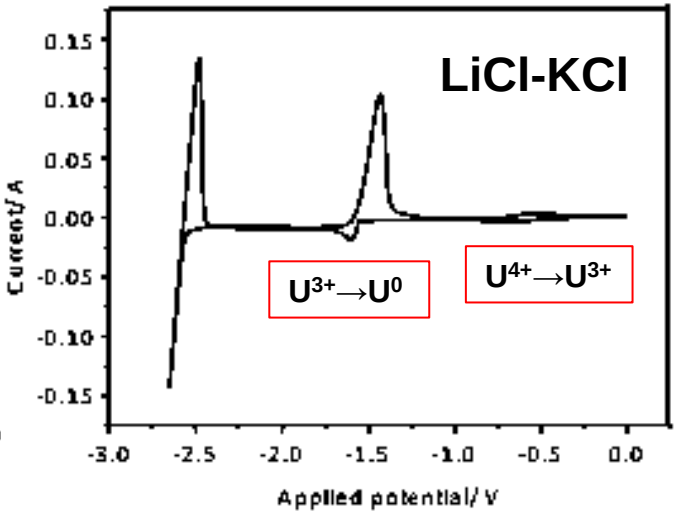


Performance of an RE exhibits strong Ni^{2+} speciation dependence of the inner electrode couple.

Determination the parameters of key elements

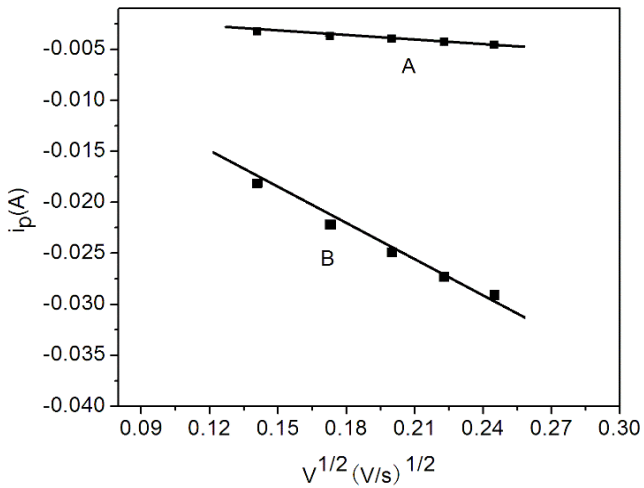






Reaction	Redox potential（V） vs. NiF_2/Ni	$D/cm^2\ s^{-1}$	Separation
$Gd^{3+}+3e\rightarrow Gd^0$	-2.02/-1.68	3.2×10^{-4}	Y
$Y^{3+}+3e\rightarrow Y^0$	-1.96/-1.91	5.4×10^{-6}	Y
$Sm^{3+}+e\rightarrow Sm^{2+}$	-1.65/-1.53	7.4×10^{-6}	N
$Eu^{3+}+e\rightarrow Eu^{2+}$	-1.07/-0.89	1.3×10^{-5}	N
$Nd^{3+}+3e\rightarrow Nd^0$	-1.95/-1.88	1.1×10^{-5}	Y
$Zr^{4+}+4e\rightarrow Zr^0$	-1.86/-1.50	2.5×10^{-6}	Y
$Th^{4+}+4e\rightarrow Th^0$	-1.91/-1.66	8.4×10^{-7}	Y
$U^{4+}+e\rightarrow U^{3+}$ $U^{3+}+3e\rightarrow U^0$	-1.42/-1.24 -1.83/-1.69	1.3×10^{-6}	Y

CV of U^{4+} and U^{3+} in FLiNaK



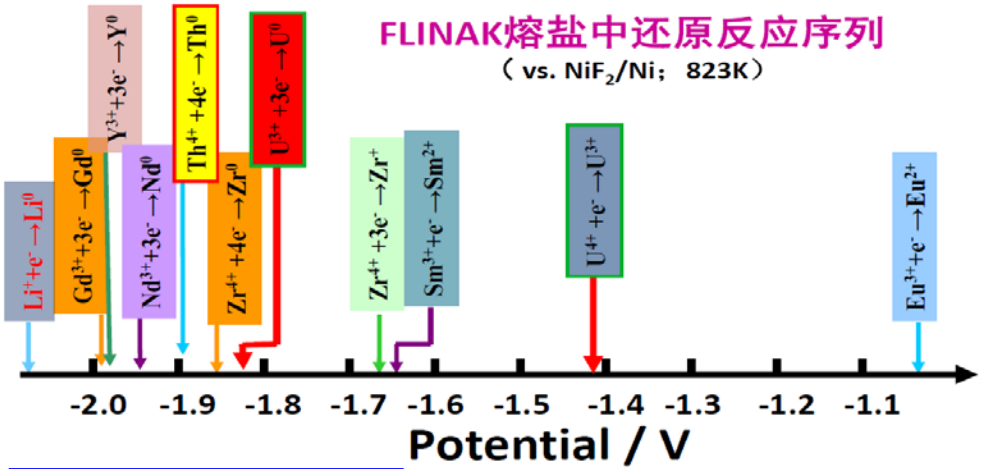
$$i_p = 0.44\,(nF)^{3/2} A C^0_{U4+} D^{1/2} v^{1/2} (RT)^{-1/2}$$

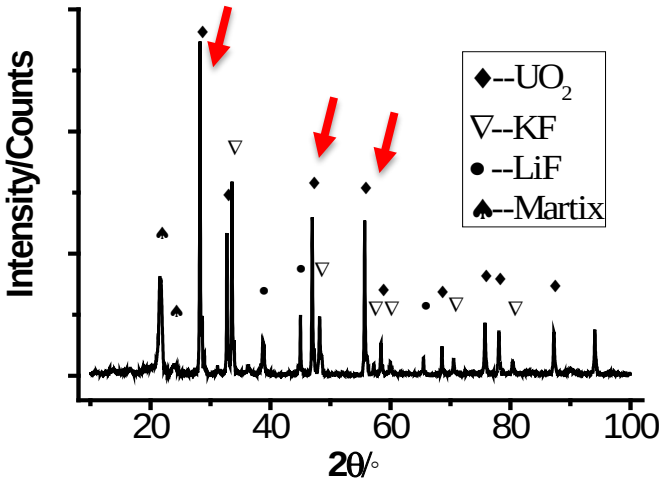
FLiNaK, 823K

$D(U^{4+}) = (4.7 \pm 0.9) \times 10^{-6}\ cm^2\ s^{-1}$

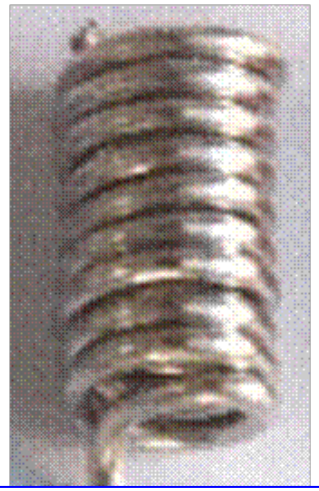
$D(U^{3+}) = (2.6 \pm 0.2) \times 10^{-6}\ cm^2\ s^{-1}$

Reduction sequence and electro-deposition of U

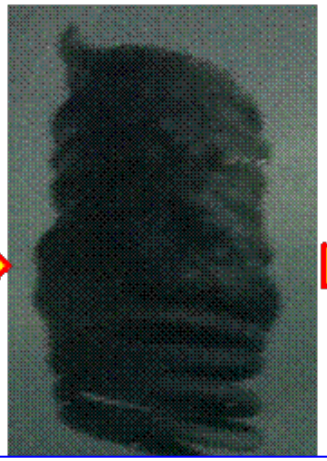




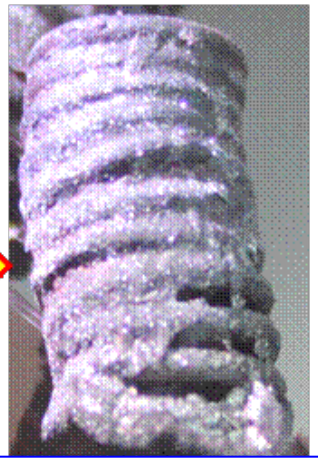
U deposition



Ni Electrode



Deposition product



Product after removal of salt

C^0_U in MS

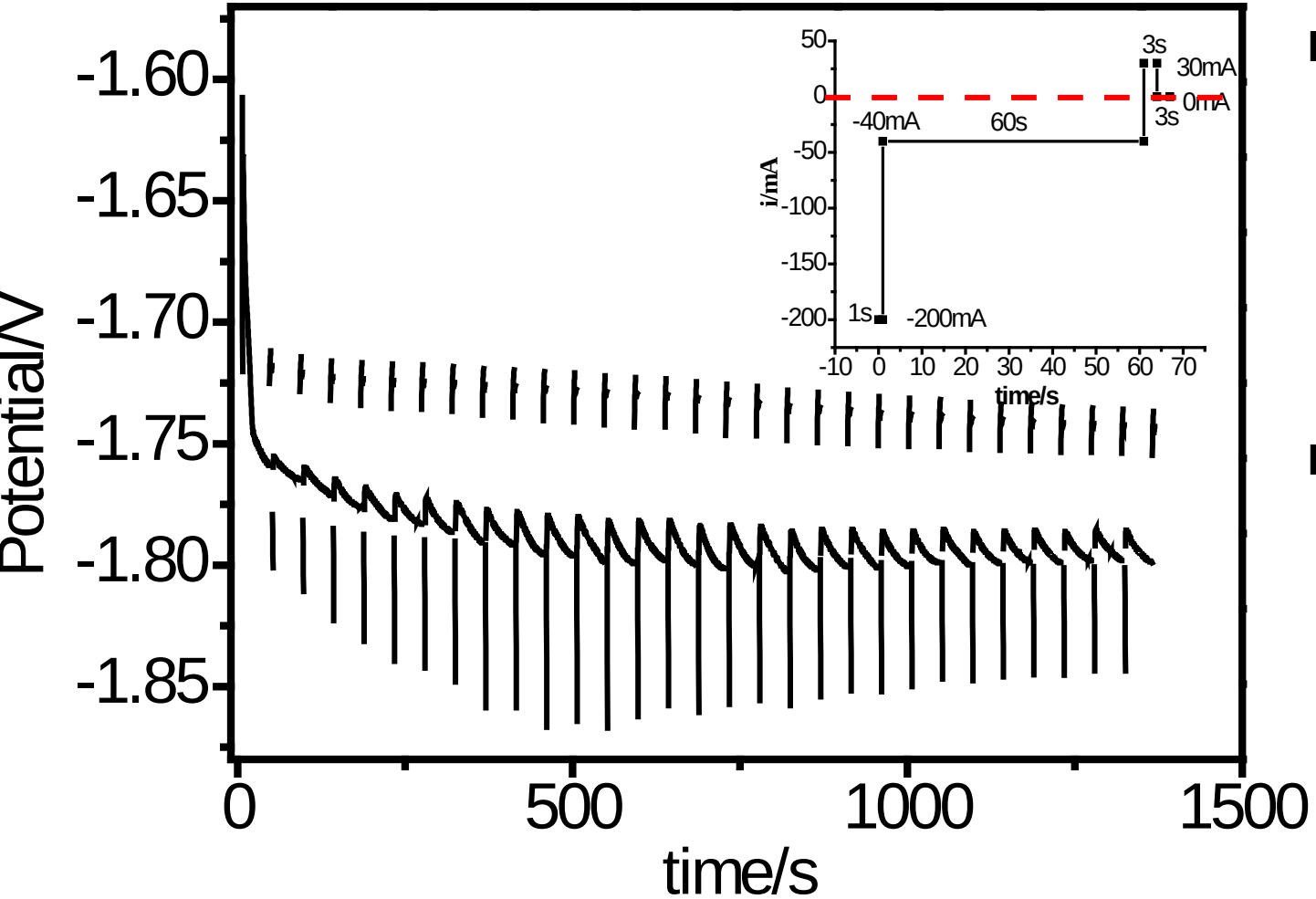
U %～ 3%

C_U in product

U %～ 30%

Advanced method for electro-deposition of U

Current pulse electrolysis



Pre-concentration

⇩

deposition

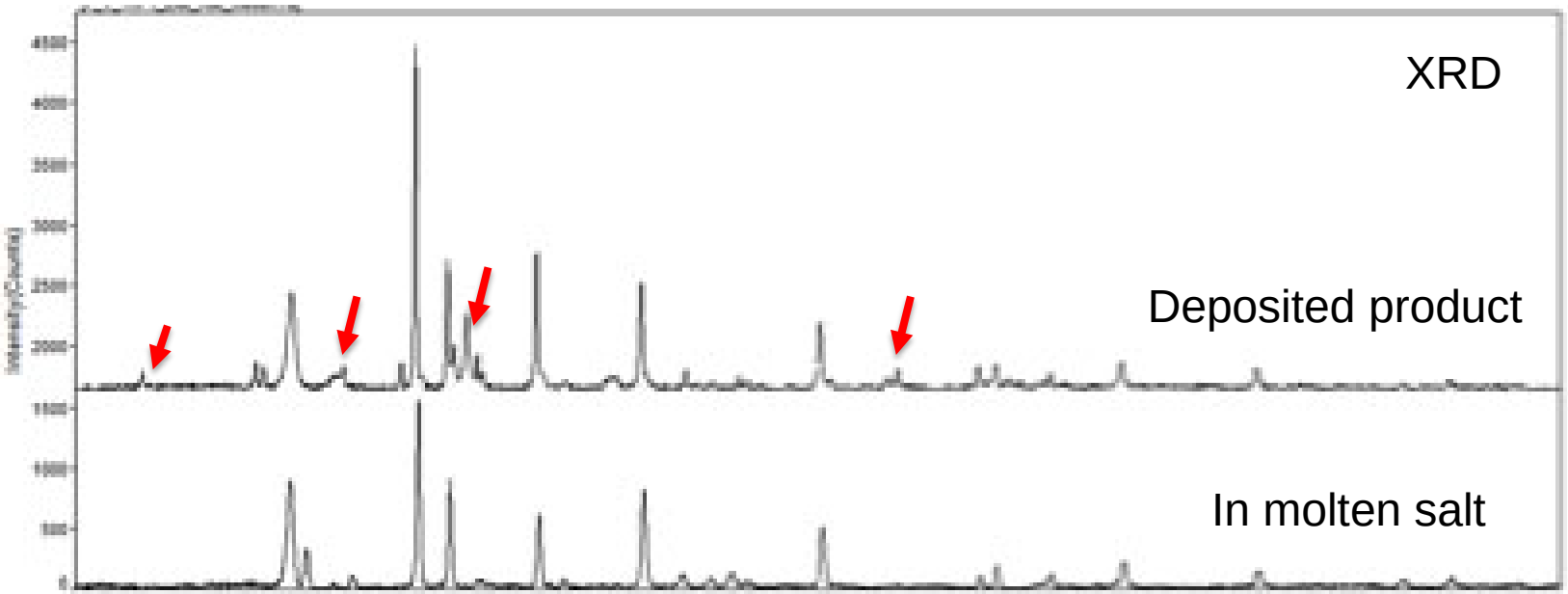
⇩

dissolving

⇩

Post-stabilization

Electro-deposition of Th in LiCl-KCl



ICP-AES

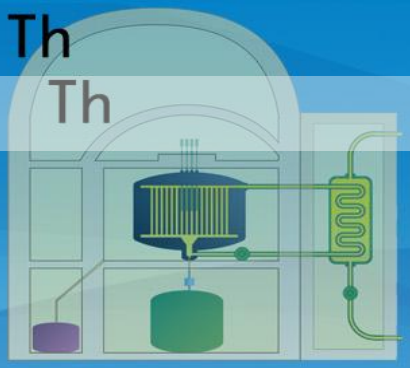
Sample	C_{Th}	C_{Th}^{0}
Deposition Product	33.46	7.48
Molten salt after electrolysis	3.83	

Summary & future work

- High performance reference electrode has been fabricated and the influence of Ni^{2+} speciation on the performance of the electrode is evaluated.
- Electrochemical behaviors of U and Th in various molten salts have been investigated and preliminary deposition of U and Th was conducted. The feasibility of recovery of U and Th was confirmed.
- Future work would be focused on
  - Improve the reliability of the measurement of fundamental data in fluoride salt.
  - Develop in-situ electrochemical method for process monitoring and TMSR salt chemistry controlling (U^{4+}/U^{3+} ratio represent the redox chemistry).
  - R&D of electro-chemical separation technique for TMSR fuel cycle as well as designing of large-scale apparatus.

Th

Th



Thank you for attention