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INVESTIGATION OF FUSED BROMIDE SALTS FOR POSSIBLE PYROPROCESSING APPLICATIONS

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Sub-titles

- Brief Background
- Experimental WORK
- Conclusions
- Goals for Next Review

Background of the present work

- Molten salt based pyroprocessing technology is critically important to the United States' Fuel Cycle Research and Development (FCRD) activities (e.g. modified fuel cycle option, spent fuel treatment mission and non-proliferation issue).

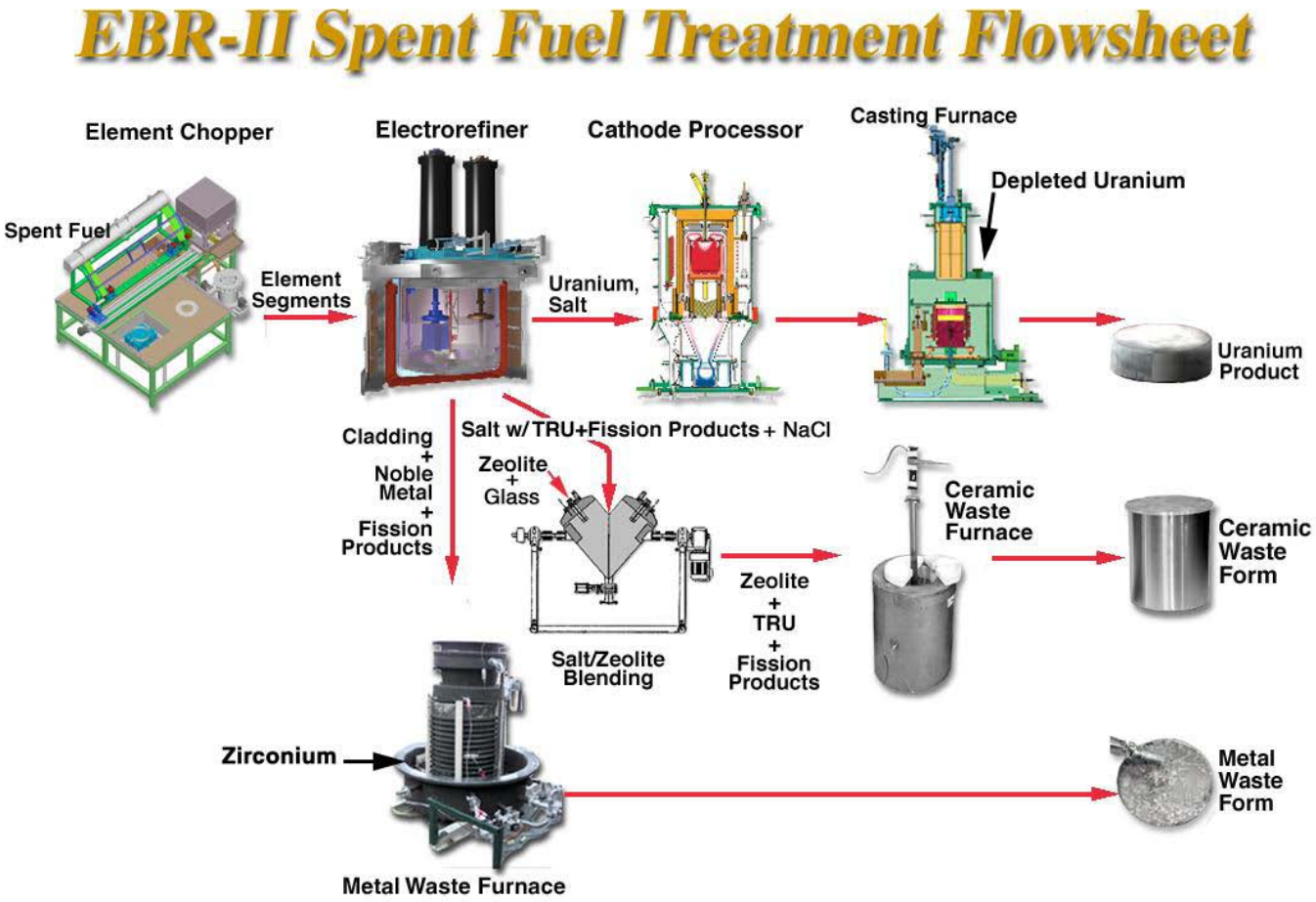
- Electrorefining is the core of the pyroprocessing technology.

- In this process, bulk of the un-used uranium is recovered from the spent nuclear fuel.

What is Electrorefining?

- Recovers uranium in the form of a dendritic mass through an electrolyte that consists of either eutectic (auxiliary) (55.8%LiCl–44.2%KCl) or equimolar NaCl–KCl/NaCl–CsCl melts, containing UCl_3.
- UCl_3 acts as a functional electrolyte to transport uranium, via anodic oxidation, from the spent fuel (anode basket) to the steel cathode via cathodic deposition.
- Impurities, associated with the spent fuel; also known as fission fragments, present in the anode basket, can be divided into two categories, viz. nobler (Zr, Mo, Fe) and baser (alkali/alkaline earth metal, lanthanides and actinides).
- Accumulation of actinides (or transuranics, TRUs) in the electrolyte depends on both the quantity and composition of the spent fuel.
- To maintain the electrolyte composition within its operating envelope, it is required to remove the TRU concentration, from time to time, in another operation.
- LCC technology, based on the chemical behavior of Cd–U–TRU system, recovers the TRUs from the electrolyte and replenishes the UCl_3.
- Effectiveness of the LCC technology has been successfully demonstrated in the engineering scale (in Mark V electrorefiner) at the INL.

Electrorefining : core of the pyrprocessing technology operation



Motivations for the present work

- Electrorefining is carried out at 500^0C and ~700^0C in the LiCl–KCl (USA) and NaCl–KCl/NaCl–CsCl melts (RIAR, Russia) respectively.

Is it possible to lower the temperatures ?

Search for alternative electrolyte system(s)!

- LCC technology does not solve the problem completely so far as the efficient removal of TRUs from the electrolyte is concerned. There is a significant carry over of lanthanides into the LCC phase.

What can be a possible solution?

Electrolysis of the actinide chlorides to deposit the individual elements on a solid cathode. Such a step shall avoid the RE carry over.

What is the problem?

Dealing with chlorine gas at high temperature can pose challenges!

Potential Solution

Bromide based salts can provide four potential advantages over the currently used chloride salts.

- Comparatively lower melting temperatures.
- Unlike chlorine, bromine is a liquid at STP. Thus, it will be easier to collect the anode gas for recycling.
- Bromine is less oxidizing as compared to chlorine.
- Help improve better separation of actinides (TRUs) from other fission products, such as lanthanides.

Any work on bromide salts?

- LiBr is being used as an absorbent in refrigeration system because of its favorable thermophysical properties.
- KBr is being used in medicine as a anti-seizure drug.
- Both chlorides and bromides salts are being used as sanitizers in spas and pools.
- Bromide (as well as chloride) salts have been extensively studied as (pitting) corrosion media for SS.
- LiBr (also LiCl) has been well-studied as flame-retardants in fabric industry.
- Electrowinning and Electrorefining data in (all) bromide based salts are not available in open literatures.
- Some data on mixture of chloride-bromide salts (LiCl-LiBr-KBr, MP: 325^{0}C) in thermal/high temperature batteries have been reported. This electrolyte offered three advantages: (i) lower operating temperature (ii) passage of relatively higher currents, as compared to the current that could be passed in the binary chloride (LiCl-KCl) electrolyte, because of higher lithium contents and (iii) better life of the battery as lower operating temperature prevents the decomposition of the cathode material (FeS_2).

Electrochemistry in bromide salts

- Extensive data on electrochemical measurements in chloride and fluoride salts available in open literatures. No such data available for bromide salts. Higher cost ?
- Some fundamental electrochemical measurements involving hydride ion in LiBr-KBr-CsBr eutectic melt is available in literatures.

(i) Eutectic ternary bromide melt has been found to be an useful electrolyte for investigating M-H systems at medium-range temperatures.

(ii) Electrochemical behavior of hydrogen ion

(iii) Electrochemical formation of Al-Li alloy

(iv) Possibility of using this melt for high power density lithium ion battery (intercalation-de-intercalation studies into/from graphite electrode at 250^0C).

(v) No studies on the binary LiBr-KBr electrolyte, presumably because of comparatively higher operating temperature.

Scope of the present investigation

- Development of the phase diagram for the following three systems.
  $LiBr-GdBr_3$; $LiBr-KBr-GdBr_3$ and $LiBr-KBr-CsBr-GdBr_3$
- Studying Fundamental electrochemistry in the binary, ternary and quaternary systems.
- Electrorefining of RE surrogates.
- Electrowinning of RE surrogates.
- Development of a suitable reference electrode (Ag/AgBr).

Advantages of the Bromide salts

Melting point (^0C) (calculated) of the eutectic compositions

Bromide Salts	Chloride Salts
56.1LiBr–18.1KBr–25CsBr – 225	51LiCl–20KCl–29CsCl – 263
57LiBr–5KBr–38RbBr – 250	55LiCl–8KCl–37RbCl – 289
57.5LiBr–19CsBr–23.5RbBr –225	56LiCl–8CsCl–36RbCl – 294
55LiBr–45RbBr – 272	63LiCl–47RbCl – 324
61.3LiBr–38.7CsBr – 274	58LiCl–42CsCl – 327
60LiBr–40KBr – 328	59.5LiCl–40.5KCl – 352

Advantages of the Bromide salts

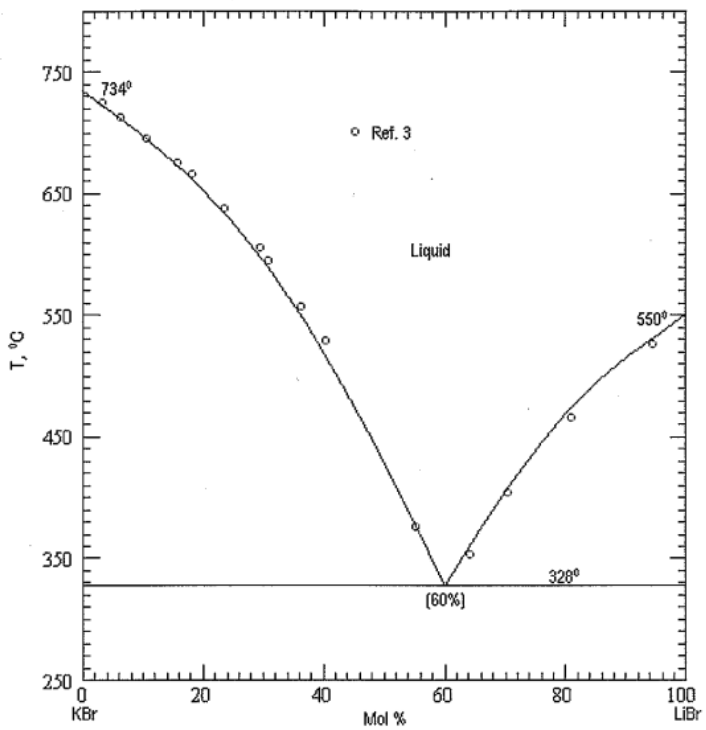


Figure 1
Binary Phase diagram of LiBr-KBr (Eutectic) system (calculated)

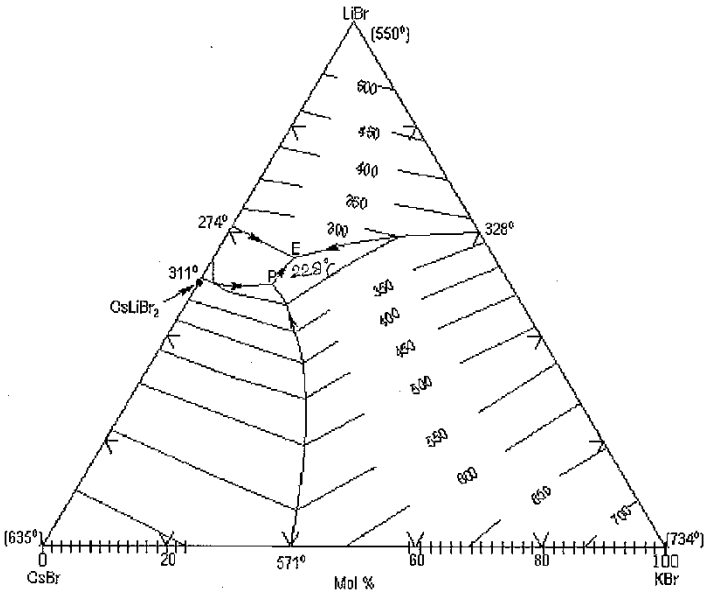


Figure 2
LiBr-KBr-CsBr (Eutectic) system (calculated)

Potential advantages of a lower operating temperature

- Wider choice of structural materials from corrosion standpoint.
- From electro-deposition standpoint, better purity, micro-crystallinity, low-temperature phases and characteristic metallographic structures.
- Reduced contamination pick-up from reactor vessel.
- Chemical and electrochemical reactions shall be different from those at higher temperatures.

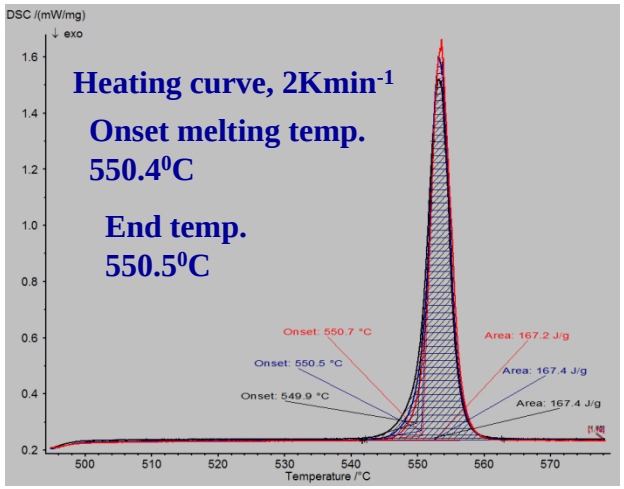
Results (I)
(Melting Point Determination and Phase diagram studies)

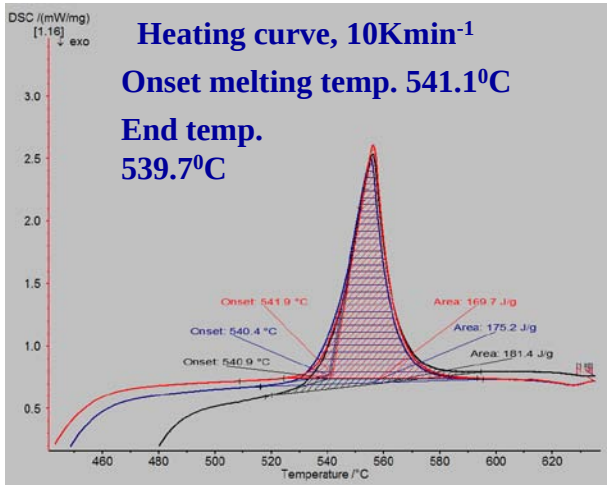
LiBr–$GdBr_3$ system (LiBr, mp. 550^0C, $GdBr_3$, mp. 770^0C)

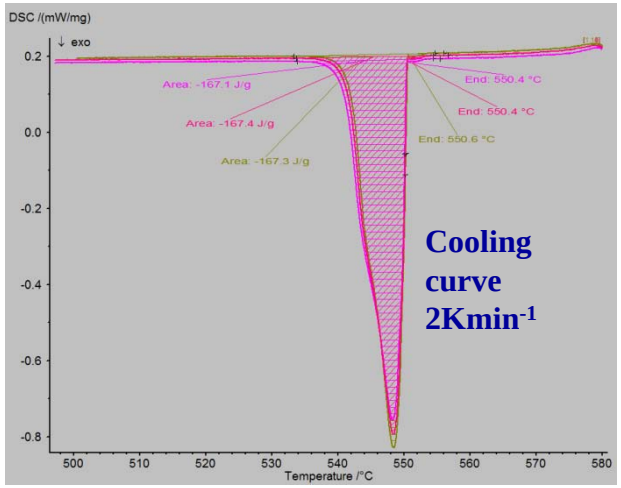
Experimental Parameters

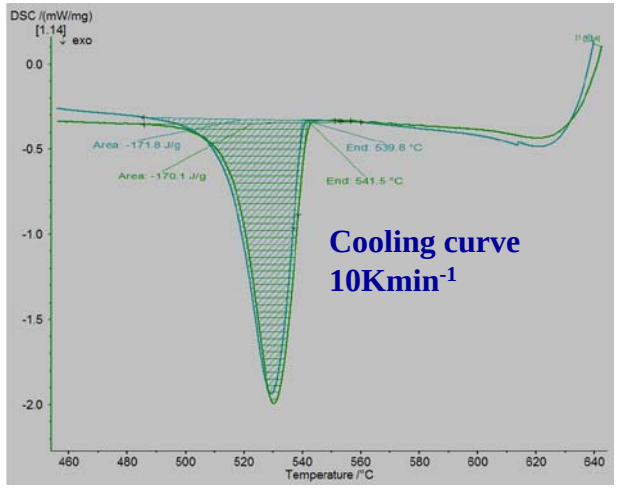
- NETZSCH STA 449 F3 (DSC)
- Pt Furnace
- SS–Au plates sealed crucibles
- Proteus Analysis Software
- Heating and Cooling rates:2, 10, 20$Kmin^{-1}$
- Sample size: ~10mg

DSC Curves for LiBr–1.08wt.% $GdBr_3$ sample







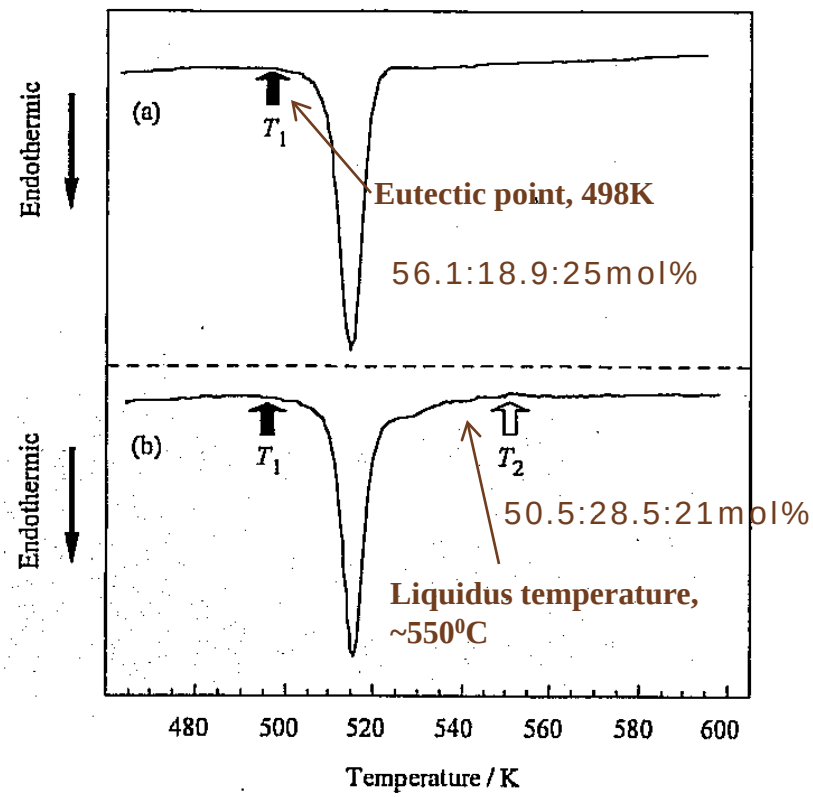


Variation in melting point with increasing $GdBr_3$ concentration, Heating rate: $2Kmin^{-1}$

Salt Composition (wt.%)	Onset Temperature (^0C)	End Temperature (^0C)
LiBr-1$GdBr_3$	550.4	550.5
LiBr-5$GdBr_3$	538.2	541.7
LiBr-10$GdBr_3$	499.0	499.9
LiBr-15$GdBr_3$	498.2	525.8
LiBr-20$GdBr_3$	489.4	492.7
LiBr-25$GdBr_3$	478.6	484.8
LiBr-30$GdBr_3$	472.4	473.5
LiBr-35$GdBr_3$	471.3	473.3
LiBr-40$GdBr_3$	442.4	456.4
LiBr-45$GdBr_3$	470.3	472.4

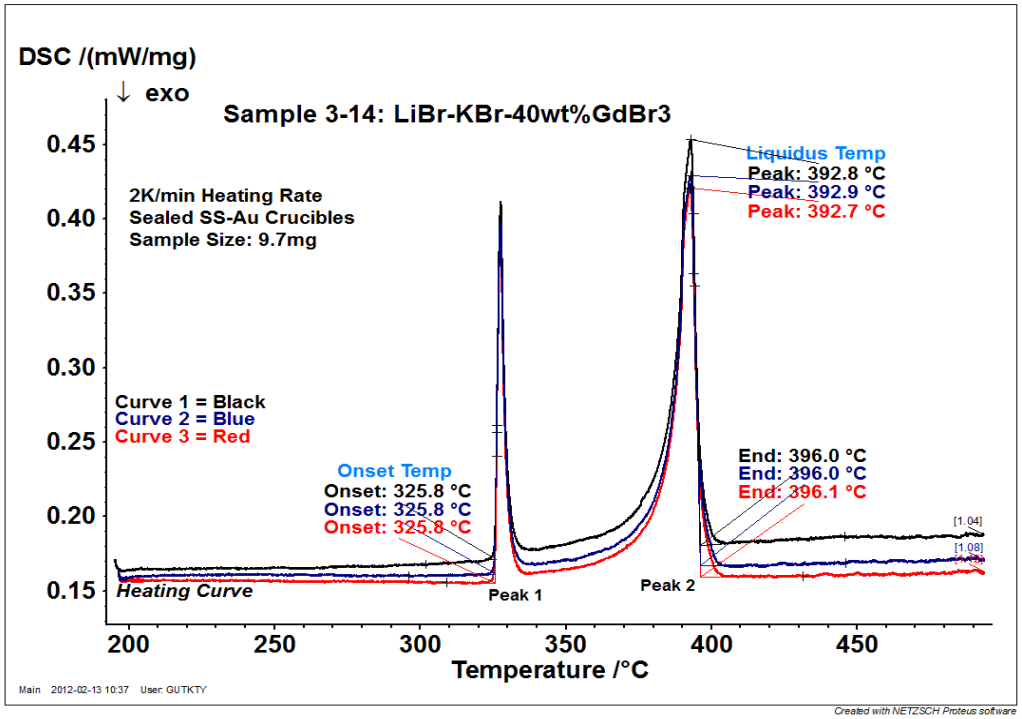
Compositions higher than 50 wt.% $GdBr_3$ have MPs higher than 550^0C, which is the max. operable temp. for the Au-coated SS crucible. These samples are currently being run in a nimonic crucible to determine the MPs for compositions, containing higher amounts of $GdBr_3$.

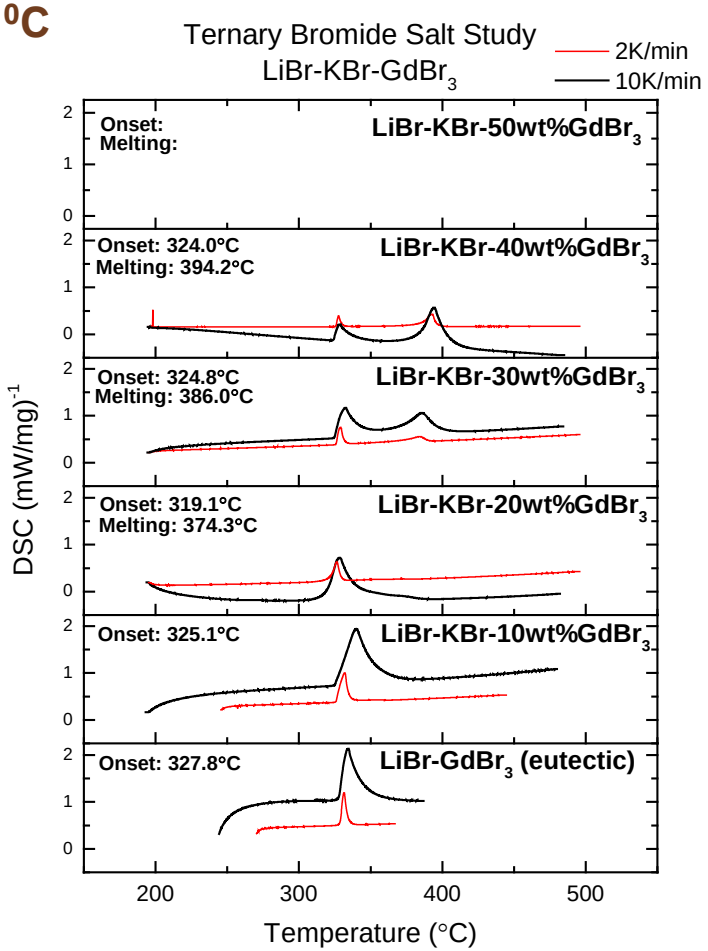
DTA curves of LiBr–KBr–CsBr melts (with two different compositions, Heating rate = 5Kmin^{-1}



Variation in melting point with increasing $GdBr_3$ concentration, Heating rates: 2, 10Kmin^{-1}

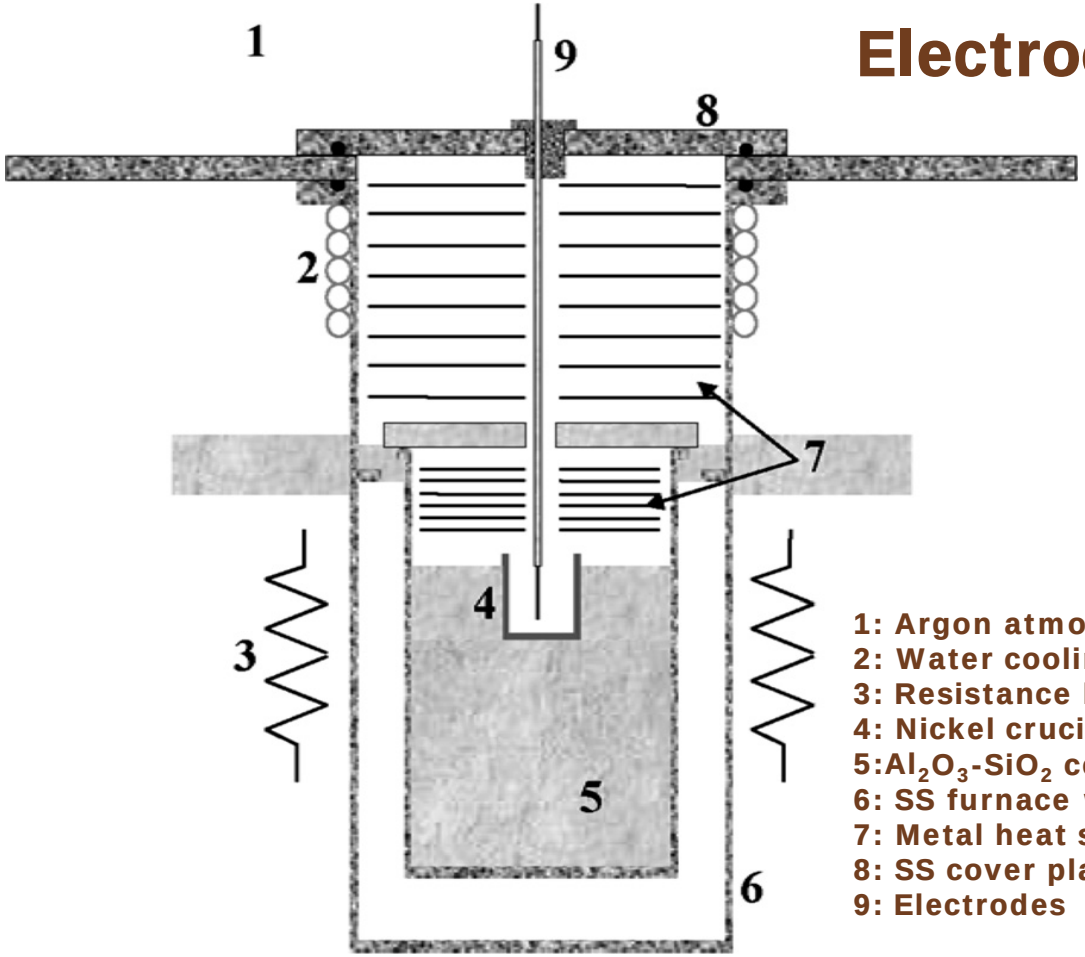
MPs, LiBr-550^{0}C, KBr-734^{0}C and $GdBr_3$-770^{0}C





MP of LiBr-KBr, containing up to 10 wt.% $GdBr_3$ has one melting temperature, which is the eutectic MP (328^{0}C) ➡ **Electrorefining can be performed at a temperature < 400^{0}C as opposed to that in a chloride melt (500^{0}C). A significant change!**

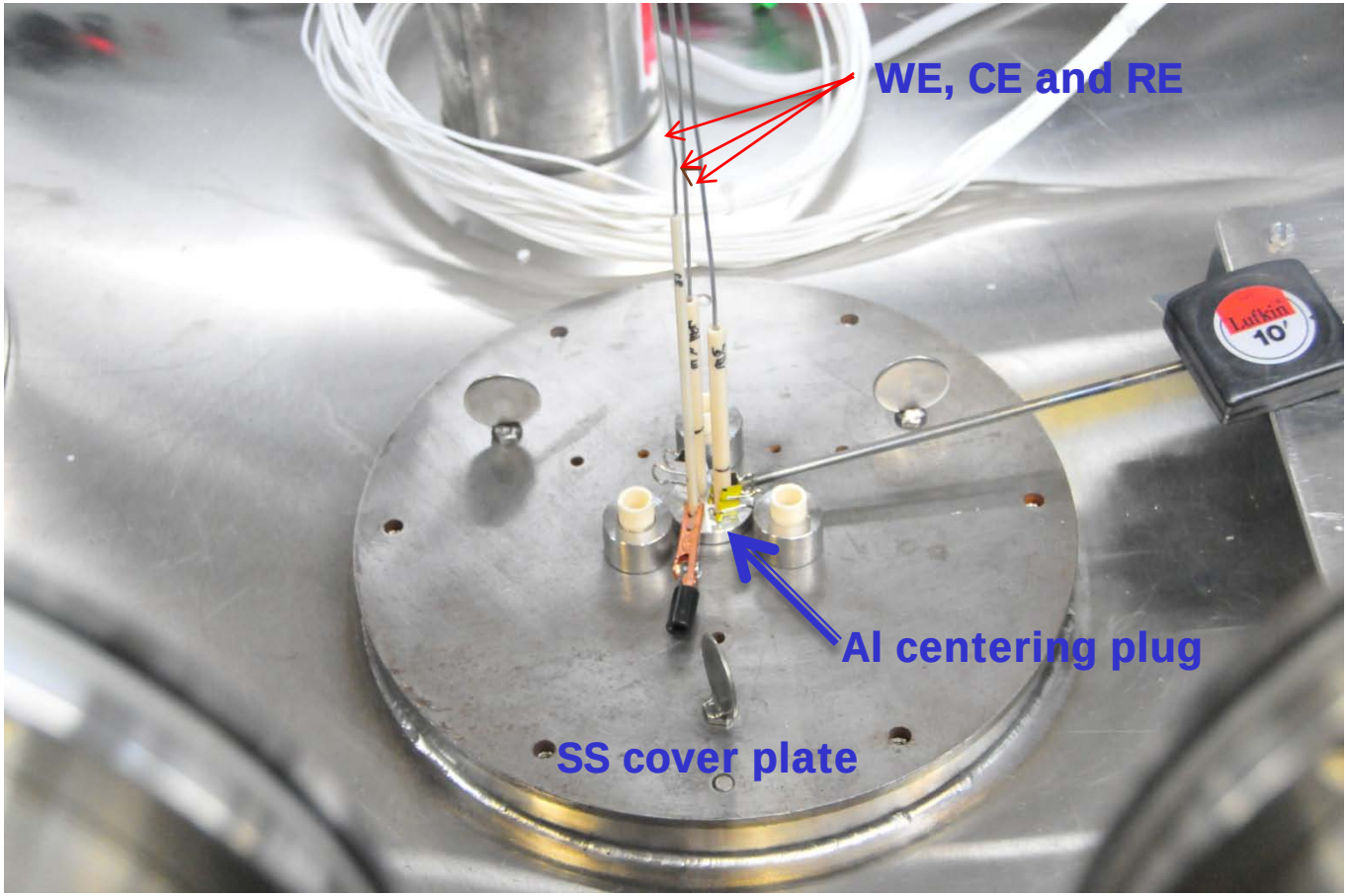
Results (II)
Electrochemical Characterizations of the melts



Electrochemical cell assembly

1: Argon atmosphere glove box, O_2<1.2ppm, H2O<0.1ppm
2: Water cooling jacket
3: Resistance heater
4: Nickel crucible, containing molten electrolyte
5:Al_2O_3-SiO_2 centering plates inside stainless steel crucible
6: SS furnace well
7: Metal heat shields
8: SS cover plate with electrode centering (aluminum) plug
9: Electrodes

Photograph showing the arrangements of SS cover plate, Al centering plug and electrode assembly



Parameters

Electrodes

- WE: Ta rod (3.175 mm dia. 100 mm long and 99.947% pure)

  W wire (1 mm dia. and 99.99% pure
- CE: Mo coil (12 turns, made of 1 mm dia. wire, 99.95% purity)

  Graphite (1mm dia. and 100 mm long)

  Glassy Carbon
- RE: Glassy carbon (1 mm dia. and 100 mm long)

1-

Crucible

Ni (Straight-walled)
Volume: 55 ml

Current collector

1.6 mm SS wire

Electrolyte quantity

80-100g

Preparation of the electrolyte

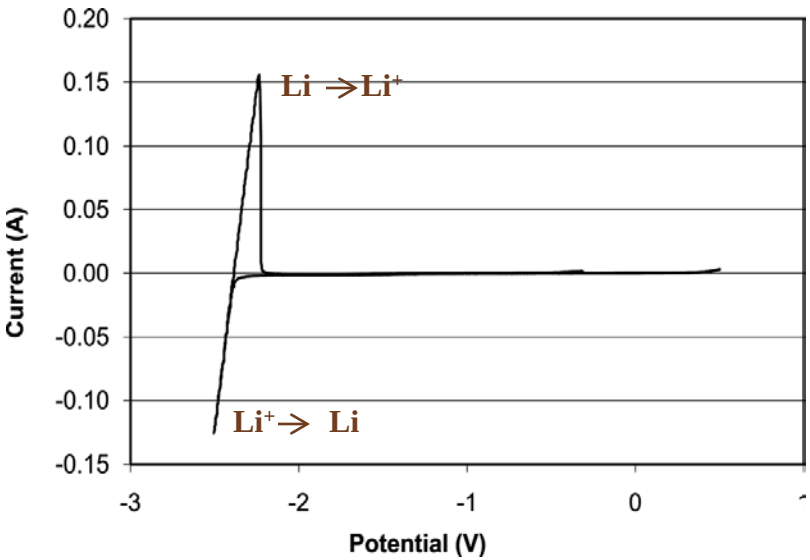
❖ Eutectic compositions of both LiBr-KBr and LiBr-KBr-CsBr were mixed at melted at 740^{0}C.

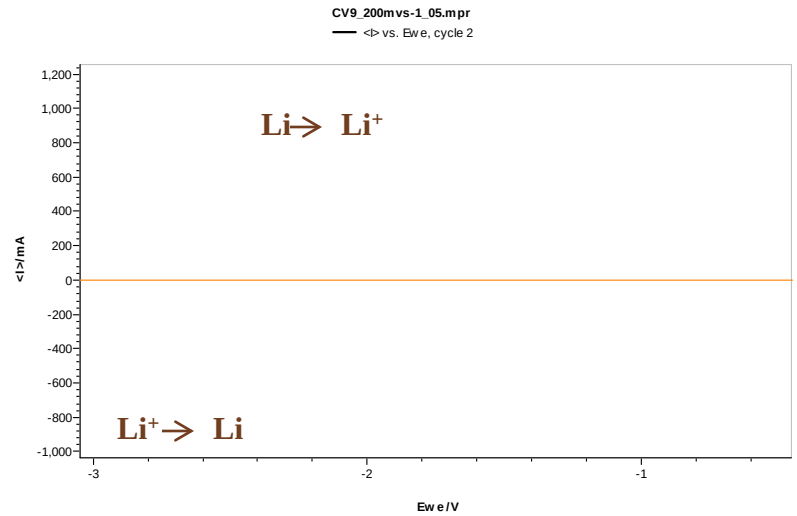
❖ Salt mixtures, containing $GdBr_3$ were first melted at 800^{0}C, cooled to room temperature, re-heated at stages, 200^{0}C and 400^{0}C respectively for 6-10h, in order to ensure complete miscibility.

Electrochemical measurements

➢ Three-electrode setup.
➢Transient electrochemical technique (CV)

Comparison of CVs , obtained in eutectic LiCl–KCl and LiBr–KBr melts respectively



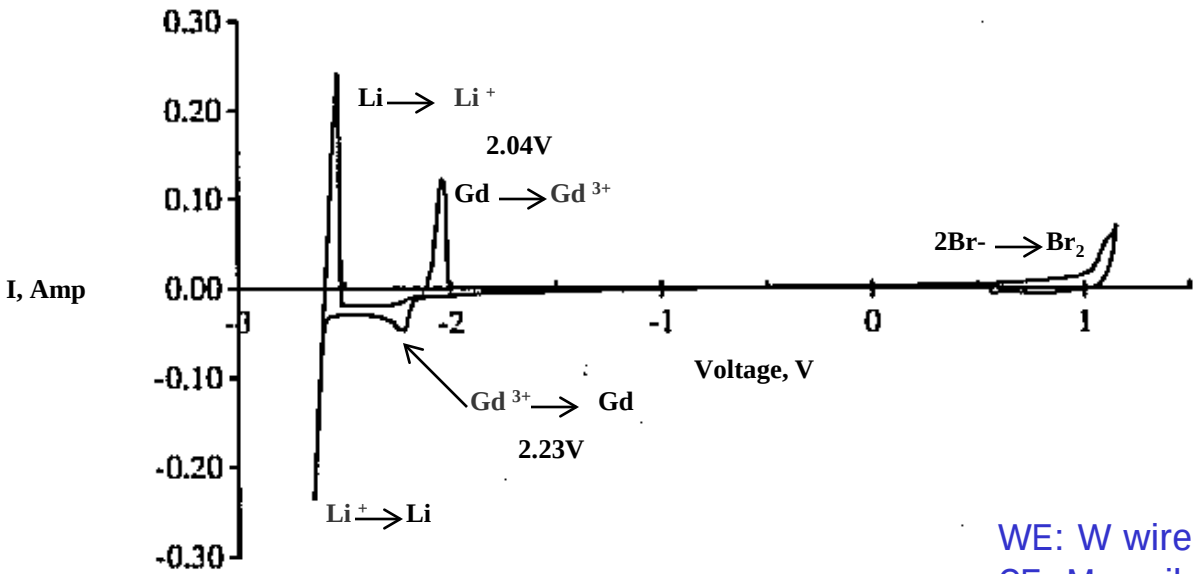


Melt:LiCl-KCl eutectic, T: 500^{0}C, WE: W wire (surface area 0.22 cm^2, CE: Mo mesh, RE: Ag/AgCl, Scan rate 0.2 V/s, Li deposition:-2.4V

Melt: LiBr-KBr eutectic, T: 400^{0}C, WE: W wire (surface area:0.22cm^2, CE: Mo coil, RE:GC, Scan rate:0.2Vs^{-1}, Li deposition: 3V, Li re-dissolution:2.53V

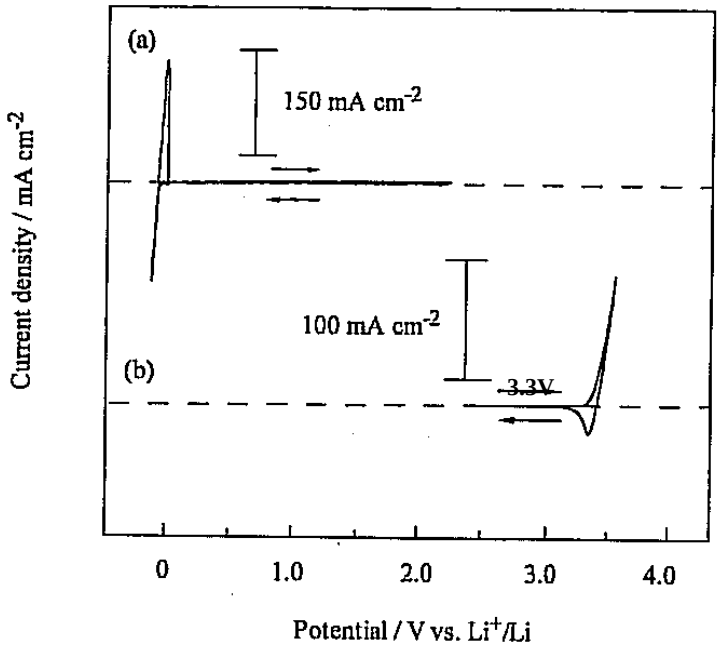
In both the cases, the melt was free of oxides/hydroxides and/or any other impurities

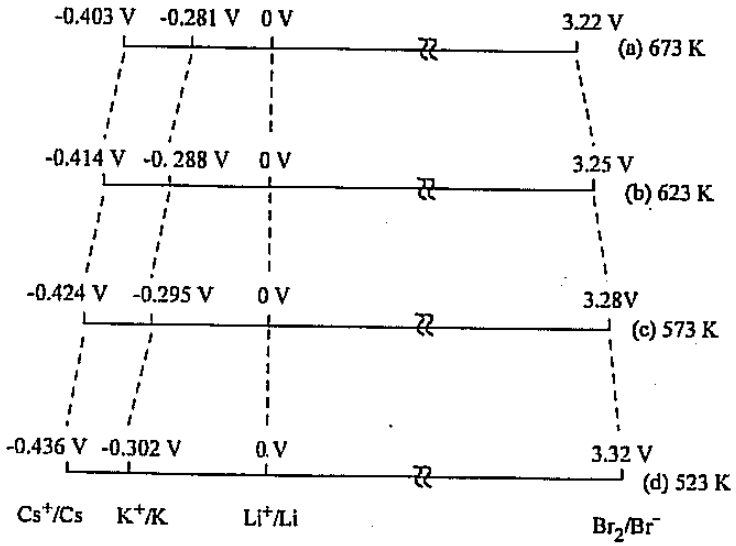
Cathodic and Anodic limits of the Electrochemical window in eutectic LiBr-KBr melt



WE: W wire (surface area- 0.352 cm^2)
CE: Mo coil
Electrolyte: LiBr-KBr-$GdBr_3$ (2.03×10^{-2} mol/kg)
Scan rate:$0.2 Vs^{-1}$
Melt temperature:400^0C

Electrochemical window in eutectic LiBr–KBr–CsBr melt, 300^{0}C





(a) WE: W wire ; CE: Mo coil RE:GC
(b) WE: W wire ; CE and RE: GC

Electrochemical potential window at different operating temperatures

Decomposition potentials of LiBr, KBr and CsBr at 300^{0}C are 3.34V, 3.68V and 3.78V respectively

Electrochemical window of the LiBr-KBr-CsBr melt

- During cathodic scan, currents were due to the deposition and dissolution of Li, K and Cs.
- The potentials of all three metals were measured.
- The potentials of K and Cs were more negative (than Li) in the beginning and they shifted to the Li potential as Li displaced K and Cs after some time.
- The voltammogram at GC electrode (during positive scan) showed one single couple at ~3.3V (at an electrolyte temperature of 300^0C), consisting of anodic and cathodic peaks. The anodic peak is due to the oxidation of bromide ion to bromine gas and cathodic peak represents the reduction of the evolved bromine to bromide ion.
- It was confirmed that the electrochemical window of the eutectic LiBr-KBr-CsBr melt is ~3.3V at 300^0C and the cathodic limit is the deposition of lithium metal.

Conclusions

- Both the binary and ternary bromide salts exhibit potentials as alternative electrolytes to an all chloride system.
- Electrorefining of RE surrogates can, in principle, be carried out at a temperature less than 400^0C.
- Potential window of the ternary electrolyte system is ~3.3V at 300^0C

Goals for Next Review

- Electrorefining and Electrowinning data of RE surrogates.
- Performance characteristics of a new RE.
- Phase diagrams of bromide salts, containing RE surrogates.