

## **Salts purification and redox potential measurement for the molten LiF-ThF<sub>4</sub>-UF<sub>4</sub> mixture**

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**Abstract** – The "dry" techniques of producing and clearing of some metals fluorides, their mixtures and cakes of a given composition obtained without usage gaseous HF for experiments under the Project ISTC #3749 are developed. The products of synthesizing and purification of oxygen-containing compounds, are studied by methods X-ray diffraction analysis, gravimetry or IR spectrometry. The experimental studies confirmed that solid NH<sub>4</sub>HF<sub>2</sub> can be efficiently used instead of an unsafe and corrosive HF gas for removal of oxygen-containing impurities from metal fluorides and for conversion of uranium and thorium dioxides to anhydrous tetrafluorides. These processes do not require expensive equipment and special measures of safety.

The electrochemical behavior of UF<sub>4</sub> solutions in a melt 77LiF-23ThF<sub>4</sub> (mole%) was studied by cyclic voltammetry. Formal analysis of the obtained dependencies showed that in our experimental conditions the recharge U(IV) to U(III) is qualitatively consistent with voltammetric criteria and can be classified as reversible. However, the results of mathematical processing of voltammograms show that the basic calculated characteristics of this reaction differ from the theoretical values corresponding one-electron process controlled by the diffusion rate. This indicates quasi-reversibility of the studied reaction.

### **A. INTRODUCTION**

To prepare the molten salt mixtures, which are to be study is scheduled in Project #3749, use fluorides of metals with a minimum content of water and impurity oxides and/or oxyfluorides. They can lead to hard-to-control changes in the chemical composition, the physico-chemical properties of the test melt, and the active surface of the electrodes and the samples, with an ultimate adverse effect on experimental results.

Most methods developed and tested at ORNL for the removal of oxide compounds from fluoride salts are based on high-temperature treatment with gas mixtures containing the toxic and corrosive hydrogen fluoride (HF). But the work with the HF gas at high temperatures requires considerable expenditures for special equipment, monitoring systems, and personnel safety. When preparing small batches of salts it is not economically justified. Therefore making and testing of laboratory "dry" techniques of producing and clearing of some metals fluorides, their mixtures and cakes of a given composition obtained without usage gaseous HF is indispensable.

Use of molten fluorides as reactor coolants & fuels is the one of the most perspective ways in the nuclear power development [1]. In this connection, special significance is attached to on-line control of the chemical composition and the redox condition of the circulating molten fluorides mixtures. A solution of these problems is a necessary condition for a safe and long MSR operation, which is largely limited by the compatibility of the container material and the molten salt fluorides mixture [2].

It was found already at early stages of MSR program at ORNL that treatment of molten fluorides by electronegative reducing metals, e.g., beryllium or zirconium depending on the solvent composition, considerably decreases the oxidizing capacity of the melts [3]. As a result, resistance of structural materials to uniform corrosion and tellurium intercrystalline corrosion can be improved. However, in MSR, when electropositive fission and corrosion products are accumulated in the fuel salt, the effect of a such fuel reducing treatment should last sufficiently long. To decrease the corrosivity of the melt, it is necessary to provide a redox buffer, which will have a considerable capacity so as to reduce oxidation impurities and maintain the melt redox potential in the required range for a long time.

The  $UF_4 / UF_3$  buffer couple was developed at ORNL within MSBR program. The  $UF_4 / UF_3$  couple was produced by reduction of molten salt mixture fuelled by  $UF_4$  with beryllium or zirconium until the required ratio  $[U(IV)]/[U(III)]$  was obtained. When the active component ( $UF_3$ ) of the buffer couple was spent for reduction of corrosive impurities, a metal rod was immersed into the melt again and was held there until the  $UF_3$  concentration returned to its initial value.

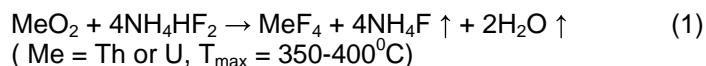
The  $[U(IV)]/[U(III)]$  ratio for molten salt mixtures containing this redox buffer couple was measured most accurately and reliably by a voltammetric analysis. Parallel spectrophotometric tests of the melt samples, which required more complicated and expensive equipment, confirmed this conclusion [4].

The voltammetric method, developed at ORNL for measuring the  $[U(IV)]/[U(III)]$  ratio in the MSR fuel salt, is based on determination of the difference between the redox potential of the melt,  $E_{EQ}$ , and the voltammetric equivalent of the standard redox potential  $E^0$  of the  $U(IV)/U(III)$  couple at  $[U(IV)] \gg [U(III)]$ . In conditions of linear voltammetry, at a stationary electrode and a reversible charge exchange of the melt-soluble oxidized and reduced forms of uranium,  $E^0$  is approximately equal to the half-wave potential  $E_{1/2}$  and corresponds to the potential in the voltammogram, at which the current accounts for 85.2% of the peak current.

A necessary condition for the use of this method is the reversibility of the process of cathode reduction of the ions  $U(IV)$  to  $U(III)$ . To determine the applicability of this method for control of redox potential in the molten salt mixture 77LiF-23ThF<sub>4</sub> (mole%) with additions of  $UF_4$  the kinetics of electroreduction of  $U(IV)$  on platinum, molybdenum and tungsten electrodes was studied.

## B. PREPARATION OF SALT MIXTURES FOR EXPERIMENTS

On preparation stage of experiments with molten salts the researches were conducted on making and testing of laboratory "dry" techniques of producing and clearing of some metals fluorides, their mixtures and cakes of a given composition obtained without usage gaseous HF. Instead of it the low-melting ammonium hydrofluoride  $NH_4HF_2$  ( $T_m \approx 125^\circ C$ ) was selected. The positive experience of usage of this compound for conversion of metals, their oxides and some salts in fluorides is described in the reviews, e.g. [5, 6]. The basis of the techniques for conversion of uranium and thorium oxides ( $UO_2$  and  $ThO_2$ ) to anhydrous tetrafluorides ( $UF_4$  and  $ThF_4$ ) with the use of  $NH_4HF_2$  formed the results of the study Wani et al [7]. When heating such mixtures proceeds successive reactions of synthesis and decomposition. The total chemical reaction can be described by equation:



The following processes realized in laboratory scales:

- production of anhydrous thorium tetrafluoride from crystalhydrate;
- production of anhydrous lithium fluoride;
- conversion of thorium dioxide to tetrafluoride;
- conversion of uranium dioxide to tetrafluoride.

Obtained anhydrous salts utilised for:

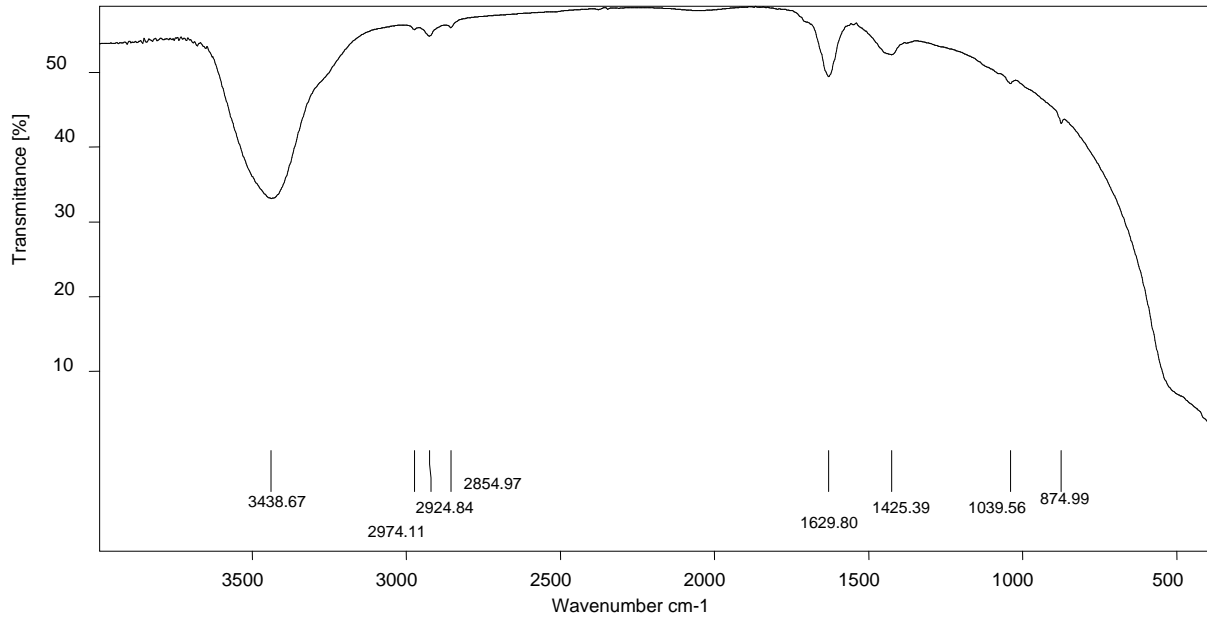
- production of the  $Li_3ThF_7$  compound;
- production of the 73LiF-27 $UF_4$  (mole %) salt cake;
- production of the 78LiF-22[ $UF_4+ThF_4$ ] (mole %) salt cake;
- production of the LiF- $UF_3$  salt cake.

A zone melting and filtration of melts through the nickel filter have used in some cases for additive clearing salt cakes from impurity. The detailed description of these processes and outcomes of the X-ray diffraction analysis of the obtained fluorides, their mixtures and salt cakes of a different composition will be submitted in the first annual report on the Project ISTC #3749.

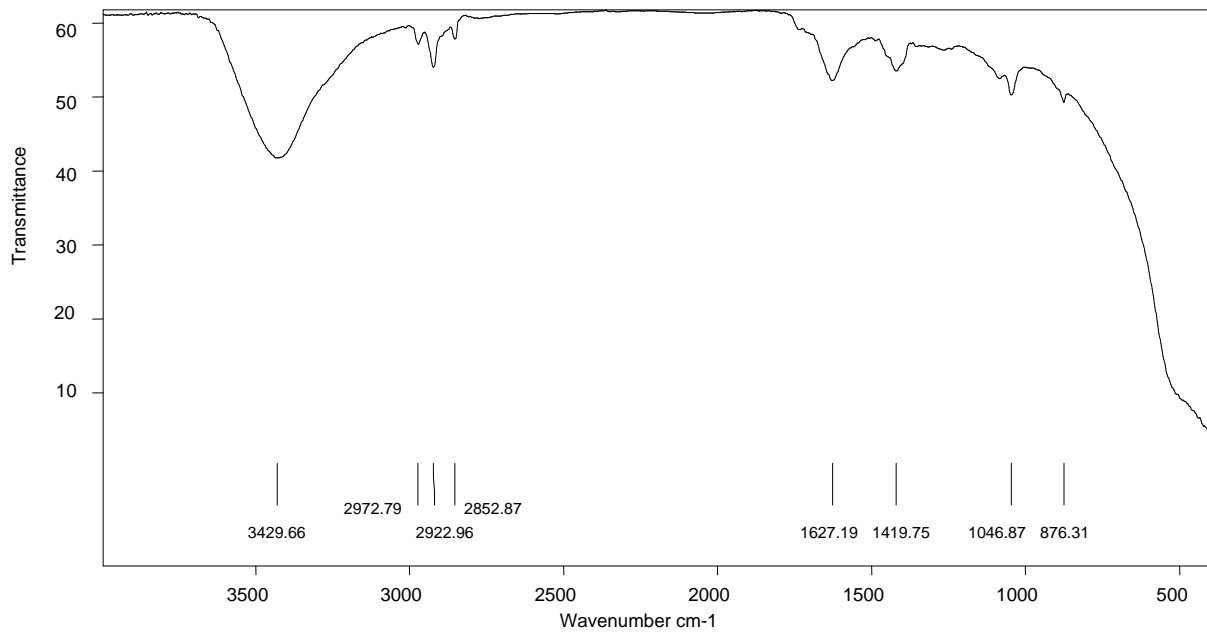
The main advantages of these methods of producing and clearing of fluorides from the oxygen-containing impurities and the conversion of oxides into fluorides are their simplicity, low cost and relative safety. Heating of reaction mixtures with  $NH_4HF_2$  done gradually to a temperature not exceeding the  $400^\circ C$  in loose closed crucible of glassy carbon in the air. With proper realization of processes intensive gassing, splashing and spraying the reaction mixtures does not occur. The disadvantage is the difficulty in obtaining isothermal throughout the volume of the reaction mixtures. Local overheating of the contents of the crucible can lead to side chemical reactions

involving oxygen. Thus in  $\text{ThF}_4$ , obtained from  $\text{ThO}_2$ , can appear an admixture  $\text{ThOF}_2$  as a pyrolysis product, and  $\text{UF}_4$  begins to oxidize up to  $\text{UO}_2\text{F}_2$ .

Because of the lack of simple and rapid methods for determining oxygen in the samples of the salts there remains the problem of monitoring the depth of their clearing of oxygen-containing impurities. An X-ray diffraction analysis does not provide a quantitative determination of their residual concentration in the final products of synthesis and processing.



**Figure 1: IR spectrum of the pellet No. 1**



**Figure 2: IR spectrum of the pellet No. 2**

Therefore IR spectrometry was utilised for analysis of samples. As an example, see Figures 1, 2. They shows the IR spectra of  $\text{Li}_3\text{ThF}_7$  salt cakes, obtained by melting purified  $\text{LiF}$  and  $\text{ThF}_4$  in an argon atmosphere, and measured on a Tensor 27 spectrometer (Bruker) in the range of wave

numbers from 4000 to 400  $\text{cm}^{-1}$ . Small crystals of KBr (650 mg) were mixed with a  $\text{Li}_3\text{ThF}_7$  powder (9 mg), the mixture was ground to a fine powder on a special device, and pellets were compacted of the powder in a vacuum. Two transparent pellets of  $\text{Li}_3\text{ThF}_7$  powders from different batches were made for the study. The pellet No. 1 contained  $\text{Li}_3\text{ThF}_7$  after its zone refining, and the pellet No. 2 had  $\text{Li}_3\text{ThF}_7$  taken from the bulk of the cake produced by the last melting so that the samples were free of the black inclusions insoluble in the melt.

The registered peaks at 3429.66 and 3438.67  $\text{cm}^{-1}$ , 1627.1 and 1629.80  $\text{cm}^{-1}$ , and 1419.75 and 1425.39  $\text{cm}^{-1}$  are commonly related to molecules of water, which is present in a particular form (crystalhydrate, dissolved, and adsorbed) in  $\text{Li}_3\text{ThF}_7$  samples. The method is highly sensitive to water, and the observed picture suggests an insignificant concentration of moisture in the samples. The peaks at 1046.87, 1039.56  $\text{cm}^{-1}$  and 876.31, 874.99  $\text{cm}^{-1}$  probably are related to low-symmetry compounds of oxygen and thorium ( $\text{ThO}_2$  or  $\text{ThOF}_2$ ). They are much larger in the spectrum of the second sample. A strong peak, which is related to a thorium compound of a higher symmetry ( $\text{Li}_3\text{ThF}_7$ ), is registered at  $\sim 800$   $\text{cm}^{-1}$  and lower. Unfortunately, the spectrometer does not allow measuring spectra in the range of wave numbers smaller than 400  $\text{cm}^{-1}$  so as to obtain a full spectral characteristic of the sample. This range can be covered by measuring Raman spectra. However, even these data are sufficient to conclude that the concentration of  $\text{ThO}_2$  or  $\text{ThOF}_2$  in the samples under study is extremely low.

To obtain quantitative information about the content of impurities in the tablets the calibration relations are required, built on the IR spectra of samples with a given content of each impurity. This complex and difficult task is the subject of special study.

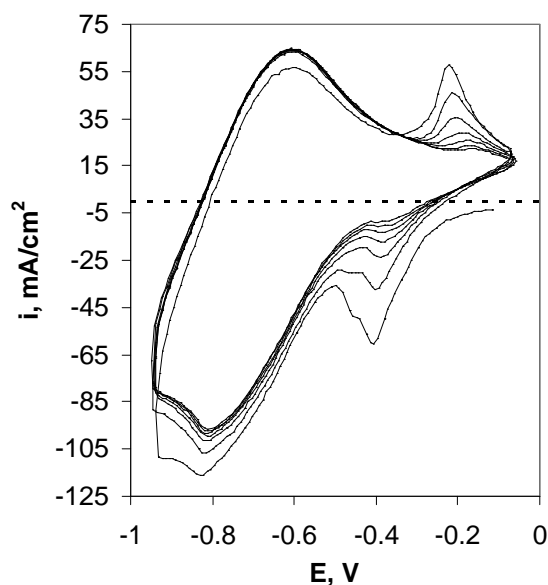
### C. VERIFICATION OF ELECTROANALYTICAL TECHNIQUE FOR REDOX POTENTIAL EVALUATION IN SALT MELTS

In order to control correctly  $[\text{U(IV)}]/[\text{U(III)}]$  ratio in molten  $\text{LiF-ThF}_4$  salt mixtures by the voltammetry, it is necessary to prove that electrochemical reaction (see Equation 2) is a reversible process governed by a simple diffusion-controlled charge transfer. Therefore the measured voltammograms should not be distorted due to side electrode processes, which hamper an exact determination of the peak current and the polarographic half-wave potential of the reaction under study. Measurement errors can increase considerably in the presence of Cr(II) ions [8], which appear in the melt corrosion products and are reduced on the working electrode in the same range of potentials as the one used for measuring the current peak of the reaction (see Equation 2). The interfering effect is also due to films on the melt surface, which can come in contact with the working electrode and alter its surface, passivation of the electrode, etc. The measurement accuracy can also be impaired by variations of the melt surface at the semisubmerged working electrode and uncontrolled fluctuations of the temperature [9].

The cyclic voltammogram of the 77LiF-23ThF<sub>4</sub> melt (mole %), which was measured on a tungsten working electrode at 600°C and a potential sweep rate of 0.1 V/s, as demonstrated Delpech et al [10], did not exhibit any electrode processes preceding reduction of  $\text{Th}^{4+}$  ions. It could be expected therefore that uranium ions will be reduced in two successive stages,

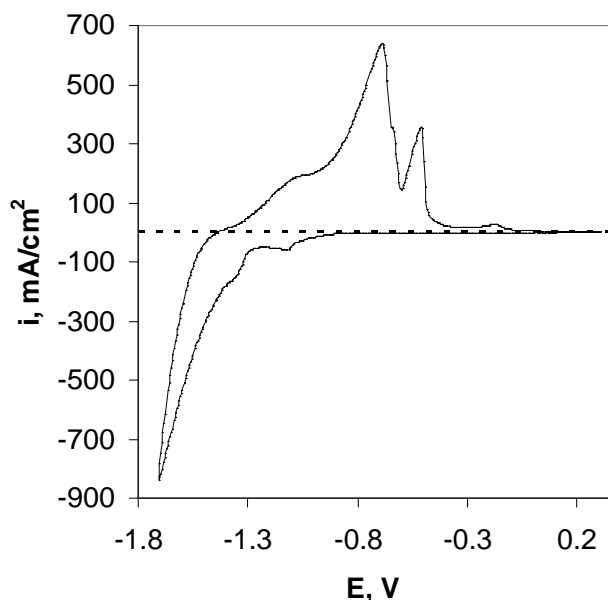


prior to deposition of thorium in the 77LiF-23ThF<sub>4</sub> melt (mole %) with an  $\text{UF}_4$  addition, which was studied by us, like in other fluoride mixtures [11-13]. An experiment showed however that an addition of  $\text{UF}_4$  to the melt-solvent was followed by side chemical reactions, leading to the formation of an electroconductive film on the surface of the working electrode and the "electrode-electrolyte-atmosphere" triple interface above the melt. As a result, immediately after the cathodic potential sweep begins, anomalously high currents are measured, see Figure 3, impeding the registration of voltammograms. The origin of these reactions is unclear, but this phenomenon probably is not different from the phenomena described in [9] and other ORNL reports.



**Figure 3: Variation of the shape of a cyclic voltammogram in eight cycles of continuous polarization. Solvent 77LiF-23ThF<sub>4</sub> (mole %) with addition of 0.34 mole % UF<sub>4</sub> prior to removal of impurities. T = 1023 K.  $\nu$  = 0.9 V/s. Pt as the reference electrode (RE); Mo as the working electrode (WR).**

To remove added UF<sub>4</sub> and impurity electropositive ions from the melt, a rod of metallic thorium with the surface area of  $\approx 4.5 \text{ cm}^2$  was introduced into the melt and was held there at T = 750°C for 3 hours. Then the melt was frozen and was used in the next experiment. A cyclic voltammogram of the thorium-treated melt is shown in Figure 4. It is seen that any processes related to reduction of electropositive impurity ions are absent in the initial section of the cathodic voltammogram. It was concluded from this observation that impurities should be carefully removed from the melts before analyzing the reversibility of the reaction (see Equation 2) and UF<sub>4</sub> should be partially reduced to UF<sub>3</sub> for recording of quality voltammograms for salt mixtures with UF<sub>4</sub> additions.



**Figure 4: Cyclic voltammogram of the solvent 77LiF - 23ThF<sub>4</sub> (mole %) with addition of 1.6 mole % UF<sub>4</sub> after treatment with metallic thorium. W as WE; Pt as RE; T = 1023 K;  $\nu$  = 0.9 V/s.**

When the melts with an addition of UF<sub>4</sub> are treated with thorium, an uncontrolled cementation of uranium on Th takes place, and, hence, the concentration of uranium fluorides dissolved in the melt decreases. Therefore, it would be preferable to reduce the melt with metallic uranium, but this process

is hard to control, too. Moreover, the surface of a uranium rod quickly becomes inactive in impurity-containing melts, and the rod should be replaced at regular intervals.

To increase the rate, at which impurities are removed from the melt, and add  $U^{3+}$  ions to the melt, weights of a ready cake, which was synthesized by reducing the  $77LiF-23UF_4$  eutectic (mole %) with metallic uranium at  $800^\circ C$ , were charged to the salt mixture through the airlock. Given the mass of uranium dissolved during reduction of the  $77LiF-23UF_4$  eutectic and knowing the weight of the cake charged to the test melt, it is possible to calculate the quantity of the reducing agent added to the melt. As an example Figure 5 presents a set of cyclic voltammograms, which were measured in one and the same melt at different sweep rates, with all other things being equal.

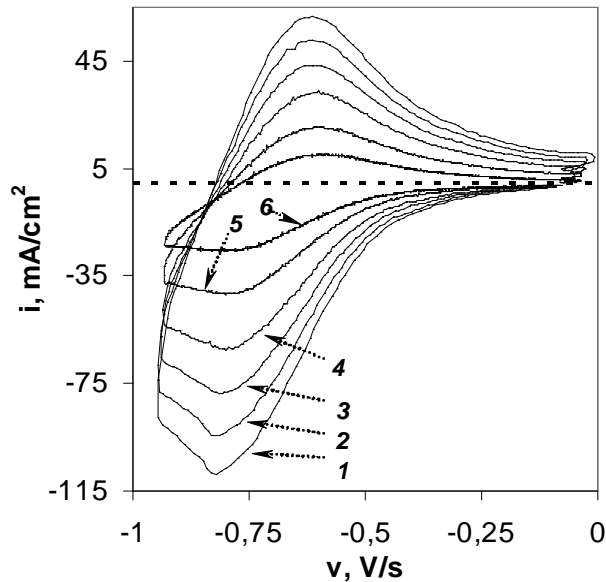


Figure 5: Effect of the potential sweep rate on the shape of voltammograms. Solvent  $77LiF-23ThF_4$  (mole %) with an addition of 0.339 mole %  $UF_4$ .  $T = 1023 K$ . Pt as RE; Mo as WE;  $v = (1) 1.0, (2) 0.8, (3) 0.6, (4) 0.4, (5) 0.2, (6) 0.08 V/s$ .

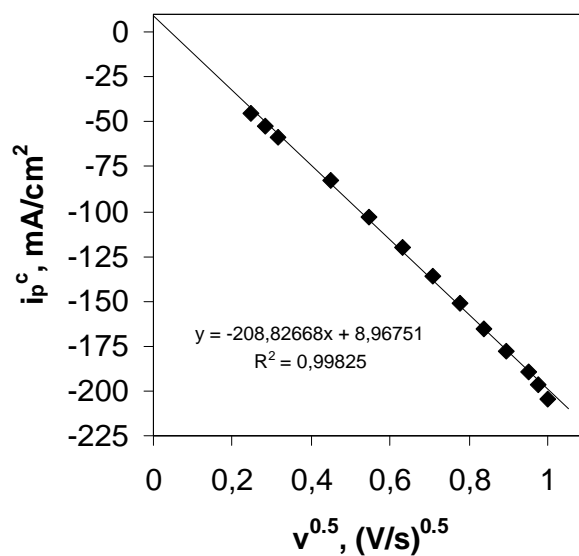
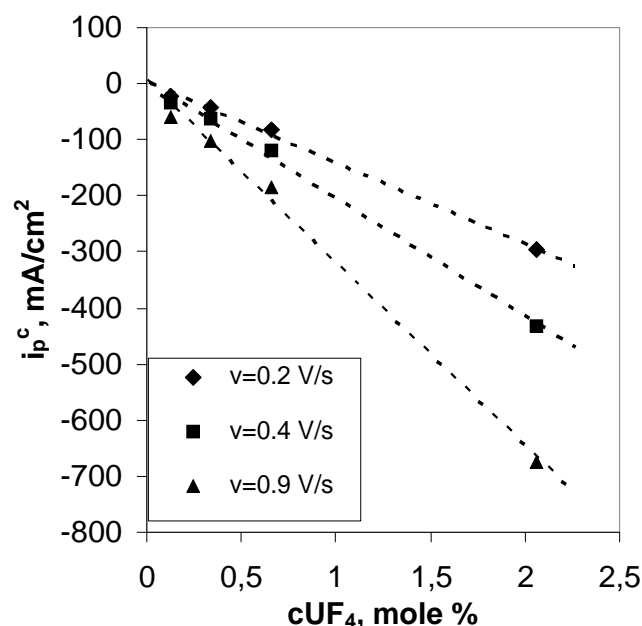


Figure 6: Effect of the potential sweep rate on the density of the cathodic peak current. Solvent:  $77LiF-23ThF_4$  (mole %) with an addition of 0.656 mole %  $UF_4$ .  $T = 1023 K$ . Pt as RE. Mo as WE.

The influence of the concentration of  $\text{UF}_4$  in the melt and the rate of potential sweep on the value of the cathodic peak current and its potential was investigated and analyzed using standard voltammetric criteria of reversibility [14]. Formal analysis of the dependencies presented in Figures 5-7 showed that in our experimental conditions the electrode reaction (see Equation 2) is qualitatively consistent with these criteria and can be classified as reversible. However, the results of mathematical processing of the cathode and the cyclic voltammograms show that the basic calculated characteristics of this reaction (the number of electrons involved in the reaction, the potential difference of cathodic current peak and half-peak, as well as cathodic and anodic current peaks) differ substantially from the theoretical values corresponding one-electron process controlled by the diffusion rate. These facts can be explained by the slow chemical reactions preceding or following an act of recharging  $\text{U(IV)}$  ions, for example, reaction formation or dissociation of fluoride complexes of uranium, the adsorption of the depolarizer or a product of recharging, and so on. In this case, using equation (2) to determine  $[\text{U(IV)}]/[\text{U(III)}]$  in the studied fluoride melt can lead to significant errors.



**Figure 7: Dependence of the density of the cathodic peak current on the  $\text{UF}_4$  concentration in the 77LiF-23ThF<sub>4</sub> (mole %) melt. T = 1023 K. Pt as RE, Mo as WE.**

## D. CONCLUSION

The experimental studies confirmed that solid  $\text{NH}_4\text{HF}_2$  can be efficiently used instead of an unsafe and corrosive HF gas for removal of oxygen-containing impurities from metal fluorides and for conversion of uranium and thorium dioxides to anhydrous tetrafluorides. These processes do not require expensive equipment and special measures of safety.

An X-ray diffraction analysis does not provide a quantitative determination of the residual concentration of oxygen-containing impurities in the final products of synthesis and processing. Special methods and instruments are required for this purpose.

The laboratory studies have revealed that well reproducible and analyzable cathodic and cyclic voltammograms are measured only in partially reduced  $\text{LiF-ThF}_4\text{-UF}_4$  melts with  $\text{UF}_3$  additions, which are freed from electropositive impurity ions.

Linearity of the dependences  $i_p^c$  vs.  $[\text{UF}_4]$  and  $i_p^c$  vs.  $v^{1/2}$ , as well as the independence of the  $E_p^c$  of  $v$  in the experiment qualitatively consistent with the voltammetric criteria of reversibility of the investigated electrode process (see Equation 2). However, its main quantitative characteristics (the number of electrons involved in the reaction, the potential difference of cathodic current peak and half-peak, as well as cathodic and anodic current peaks) differ substantially from the theoretical values corresponding to the one-electron process of recharging with a diffusion control. This indicates quasi-reversibility reaction (2).

Platinum, tungsten or molybdenum can be used as the material of the reference and working electrodes. If the electrodes are made of different materials, the thermal emf affects the results of potentiometric and voltammetric measurements.

## Acknowledgements

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# **Salts purification and redox potential measurement for the molten $\text{LiF-ThF}_4\text{-UF}_4$ mixture**

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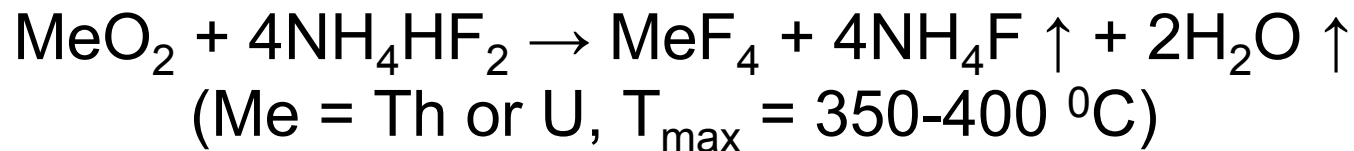
## The "dry" techniques for production and purification of metals fluorides with $\text{NH}_4\text{HF}_2$

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- To prepare the molten salt mixtures for #3749 task, the use initial metals fluorides with minimum water / oxides and/or oxyfluorides content is required.
- Most methods developed and tested for the removal of oxide compounds from fluoride salts are based on high-temperature treatment by HF containing mixtures .
- Operations with HF at high temperatures requires considerable expenditures for special equipment, monitoring systems and safety.

## The "dry" techniques for production and purification of metal fluorides with $\text{NH}_4\text{HF}_2$

- Instead of HF the low-melting ammonium hydrofluoride  $\text{NH}_4\text{HF}_2$  ( $T_m \approx 125^\circ\text{C}$ ) was selected.
- The basis for conversion of  $\text{UO}_2$  and  $\text{ThO}_2$  to anhydrous  $\text{UF}_4$  and  $\text{ThF}_4$  with  $\text{NH}_4\text{HF}_2$  is formed by **Wani et al.\***
- When heating such mixtures proceeds successive reactions of synthesis and decomposition.
- The total chemical reaction can be described by equation given below:



\*R. N. Wani et al. *J. Fluor. Chem.*, 44 2 177 (1989).



## The "dry" techniques for production and purification of metals fluorides with $\text{NH}_4\text{HF}_2$

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The following processes were realized :

- production of anhydrous thorium tetrafluoride from crystallohydrate;
- production of anhydrous lithium fluoride;
- conversion of thorium dioxide to tetrafluoride;
- conversion of uranium dioxide to tetrafluoride.

Obtained anhydrous salts utilized for:

- production of the  $\text{Li}_3\text{ThF}_7$  compound;
- production of the 73LiF-27 $\text{UF}_4$  (mole %) salt cake;
- production of the 78LiF-22[ $\text{UF}_4 + \text{ThF}_4$ ] (mole %) salt cake;
- production of the LiF- $\text{UF}_3$  salt cake.

Zone melting and filtration of melts through the nickel filter have used for additive salt purification.

# IR spectra of $\text{Li}_3\text{ThF}_7$

## Before zone melting

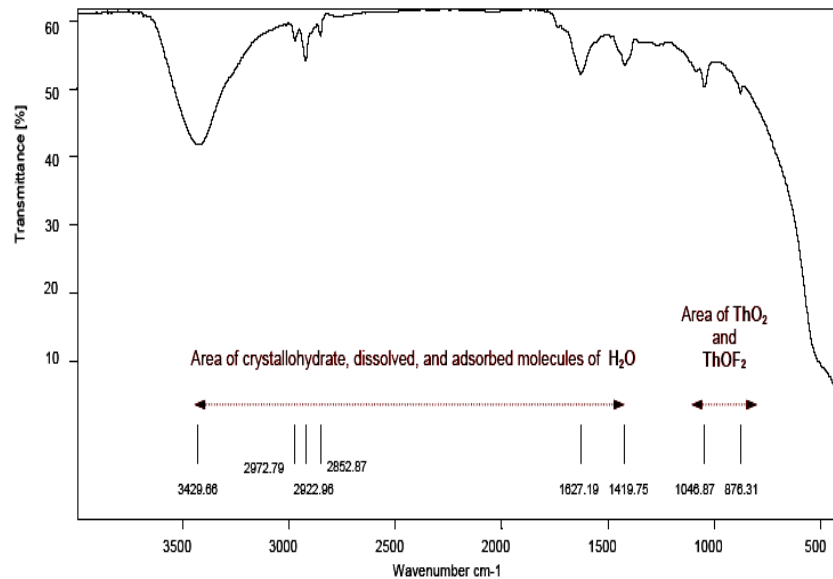


Figure 1: IR spectrum of the pellet with  $\text{Li}_3\text{ThF}_7$  cake

## After zone melting

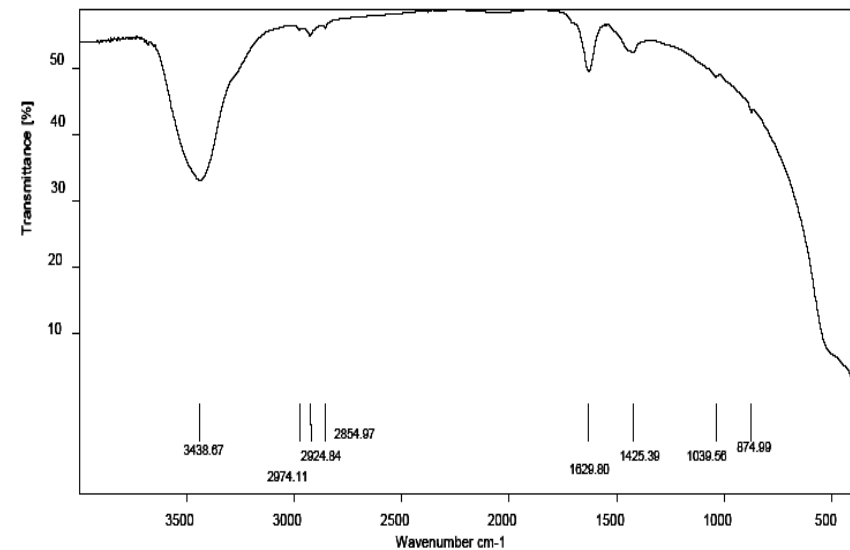


Figure 2: IR spectrum of the pellet with  $\text{Li}_3\text{ThF}_7$  cake after its zone refining


The experimental studies confirmed that solid  $\text{NH}_4\text{HF}_2$  can be efficiently used for purification of metal fluorides from oxygen-containing impurities and for conversion of uranium and thorium dioxides to anhydrous tetrafluorides. Note, that these processes do not require expensive equipment and special measures of safety.



# Verification of electroanalytical technique for redox potential evaluation in salt melts

- The  $\text{UF}_4/\text{UF}_3$  buffer couple was developed within ORNL MSBR program. It was produced by reduction of molten salt mixture fuelled by  $\text{UF}_4$  with beryllium or zirconium until the required ratio  $[\text{U(IV)}]/[\text{U(III)}]$  was obtained. When the active component ( $\text{UF}_3$ ) of the buffer couple was spent for reduction of corrosive impurities, a metal rod was immersed into the melt again and was held there until the  $\text{UF}_3$  concentration returned to its initial value.
- The  $[\text{U(IV)}]/[\text{U(III)}]$  ratio for molten salt mixtures containing this redox buffer couple was measured most accurately and reliably by a voltammetric analysis. Parallel spectrophotometric tests of the melt samples, which required more complicated and expensive equipment, confirmed this conclusion.
- The voltammetric method, developed at ORNL for measuring the  $[\text{U(IV)}]/[\text{U(III)}]$  ratio in the fuel salt, is based on determination of the difference between the redox potential of the melt,  $E_{\text{EQ}}$ , and the voltammetric equivalent of the standard redox potential  $E^0$  of the  $\text{U(IV)}/\text{U(III)}$  couple at  $[\text{U(IV)}] \gg [\text{U(III)}]$ . In conditions of linear voltammetry at a stationary electrode and a reversible charge transfer of the melt-soluble oxidized and reduced forms of uranium,  $E^0$  is approximately equal to the half-wave potential  $E_{1/2}$  and corresponds to the potential in the voltammogram, at which the current accounts for 85.2% of the peak current.

# Verification of electroanalytical technique for redox potential evaluation in salt melts



A necessary condition for the use of this method is the reversibility of the process of cathode reduction of the ions U (IV) to U(III). To determine the applicability of this method for control of redox potential in the molten salt mixture 77LiF-23ThF<sub>4</sub> (mole%) with additions of UF<sub>4</sub> the kinetics of electroreduction of U(IV) on platinum, molybdenum and tungsten electrodes was studied.

To determine the stage, controlling the rate of the investigated electrode process, we need well reproducible voltammograms. They should not be distorted due to side electrode processes, which hamper an exact determination of the peak current and the polarographic half-wave potential of the reaction under study.

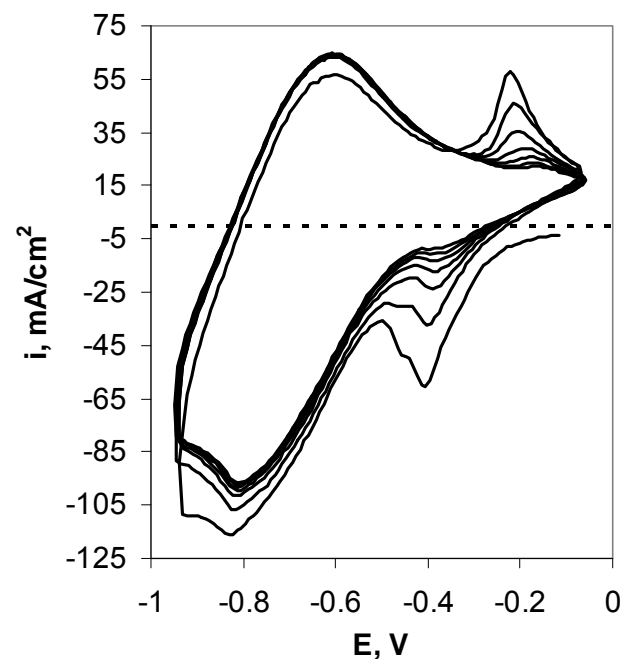
The ORNL reports shows, that measurement errors can increase considerably in the presence of Cr(II) ions, which appear in the melt corrosion products and are reduced on the working electrode in the same range of potentials as the one used for measuring the current peak of the reaction.

The interfering effect is also due to films on the melt surface, which can come in contact with the working electrode and alter its surface, passivation of the electrode, etc.

The measurement accuracy can also be impaired by variations of the melt surface at the semi-immersed working electrode and uncontrolled fluctuations of the temperature.

## Variation of the shape of a cyclic voltammogram in eight cycles of continuous polarization.

An addition of  $\text{UF}_4$  to the melt-solvent was followed by side chemical reactions, leading to the formation of an electroconductive film on the surface of the working electrode and the "electrode-electrolyte-atmosphere" triple interface above the melt. As a result, immediately after the cathodic potential sweep begins, anomalously high currents are measured, impeding the registration of voltammograms. The origin of these reactions is unclear, but this phenomenon probably is not different from the phenomena described in ORNL reports.



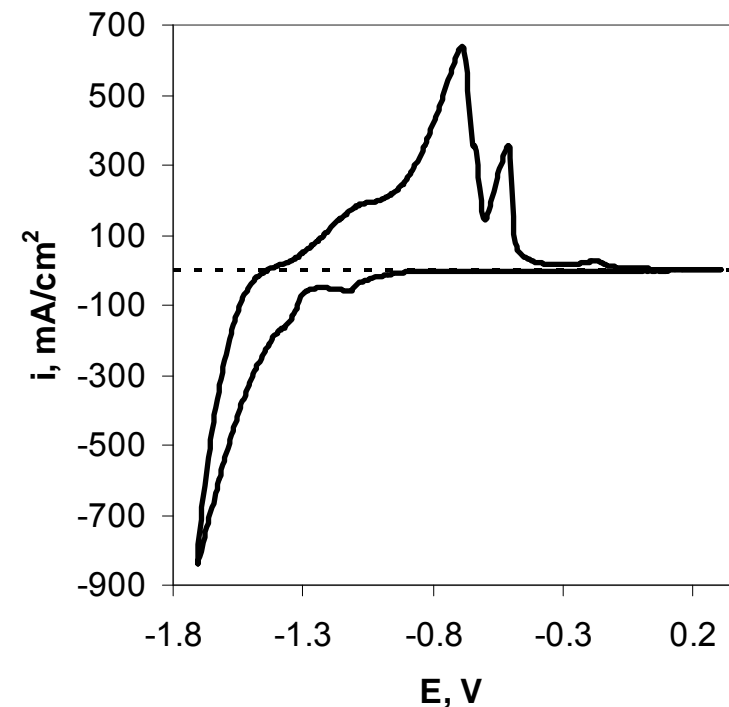
**T = 1023 K. v = 0.9 V/s.**  
**Pt as the reference electrode (RE);**  
**Mo as the working electrode (WR).**



## Cyclic voltammogram of $77\text{LiF} - 23\text{ThF}_4$ with addition 1.6 mole % $\text{UF}_4$ after treatment with metallic thorium

To remove added  $\text{UF}_4$  and impurity electropositive ions from the melt, a rod of metallic thorium with the surface area of  $\approx 4.5 \text{ cm}^2$  was introduced into the melt and was held there at  $T = 750^\circ\text{C}$  for 3 hours. Then the melt was frozen and was used in the next experiment. A cyclic voltammogram of the thorium-treated melt is shown in Figure. It is seen that any processes related to reduction of electropositive impurity ions are absent in the initial section of the cathodic voltammogram. It was concluded from this observation that impurities should be carefully removed from the melts before analyzing the reversibility of the reaction and  $\text{UF}_4$  should be partially reduced to  $\text{UF}_3$  for recording of quality voltammograms for salt mixtures with  $\text{UF}_4$  additions.

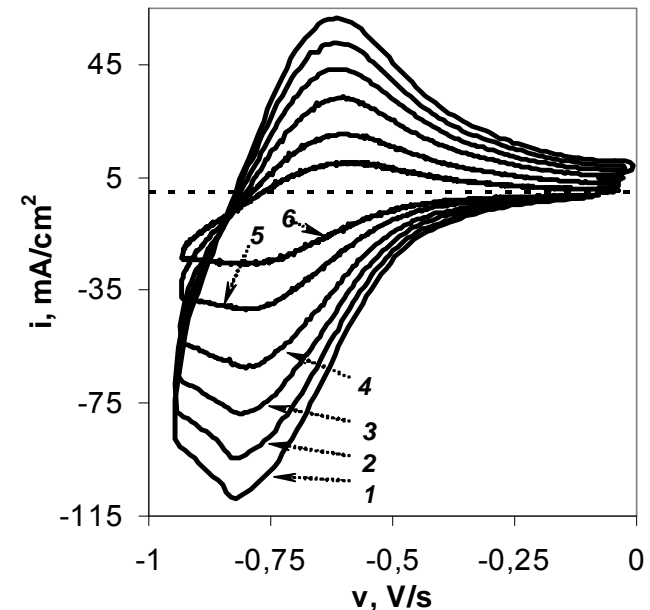
W as WE; Pt as RE;  $T = 1023 \text{ K}$ ;  
 $v = 0.9 \text{ V/s}$ .



## Effect of the potential sweep rate on the shape of voltammograms

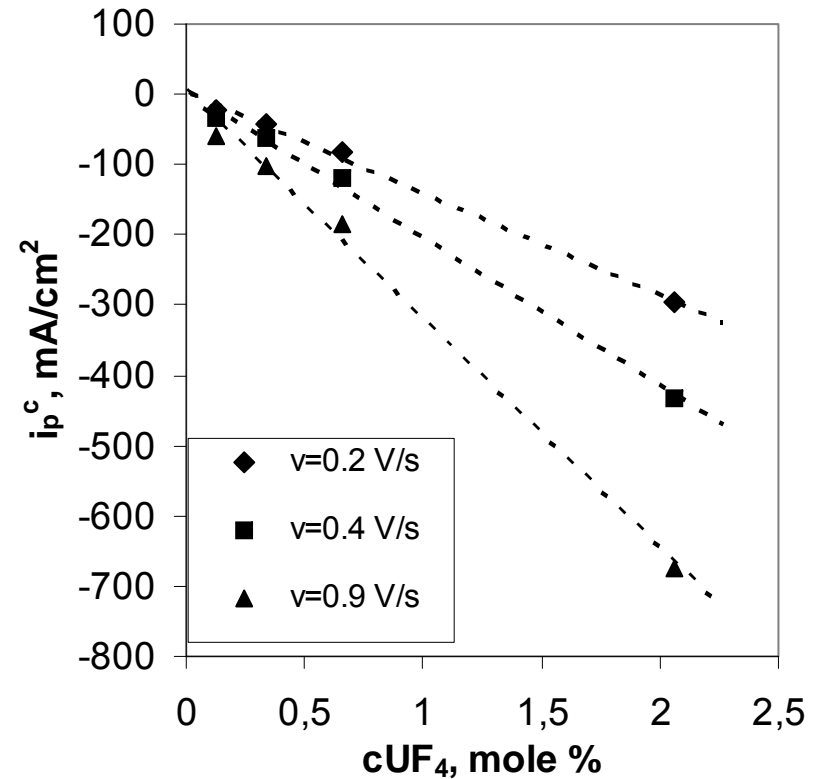
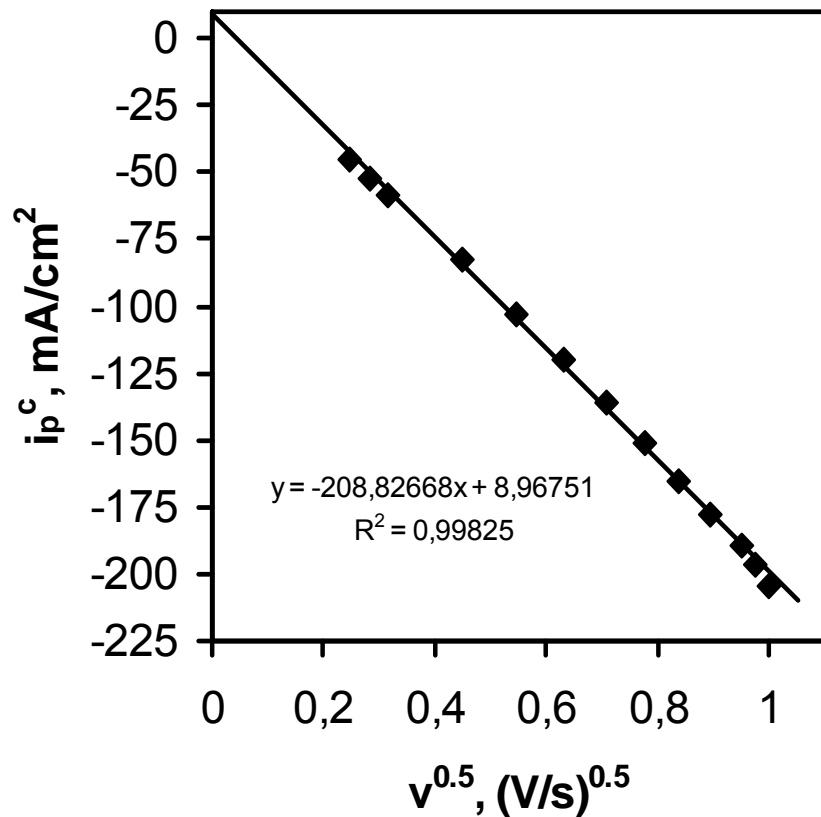
To increase the rate, at which impurities are removed from the melt, and add  $U^{3+}$  ions to the melt, weights of a ready cake, which was synthesized by reducing the 77LiF-23UF<sub>4</sub> eutectic (mole %) with metallic uranium at 800°C, were charged to the salt mixture through the gas lock. Given the mass of uranium dissolved during reduction of the 77LiF-23UF<sub>4</sub> eutectic and knowing the weight of the cake charged to the test melt, it is possible to calculate the quantity of the reducing agent added to the melt.

As an example this figure presents a set of cyclic voltammograms, which were measured in one and the same melt at different sweep rates, with all other things being equal.



**Solvent 77LiF-23ThF<sub>4</sub> (mole %) with an addition of 0.34 mole % UF<sub>4</sub>.  
T = 1023 K. Pt as RE; Mo as WE;  
v = (1) 1.0, (2) 0.8, (3) 0.6, (4) 0.4, (5) 0.2, (6) 0.08 V/s.**

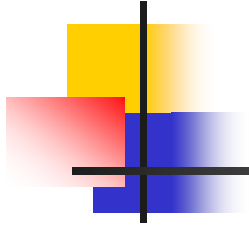
# The influence of the concentration of $\text{UF}_4$ in the melt and the rate of potential sweep on the value of the cathodic peak current and its potential





# Conclusions

- The electrochemical behavior of  $\text{UF}_4$  additions (from 0.1 till to 1.6 mole%) in 77LiF-23ThF<sub>4</sub> (mole%) melt was studied by cyclic voltammetry.
- The laboratory studies have revealed that well reproducible and analyzable cathodic and cyclic voltammograms can be measured only in partially reduced LiF-ThF<sub>4</sub>-UF<sub>4</sub> melts containing UF<sub>3</sub>, which are free from electropositive impurity ions.
- The studied electrochemical reaction is one-electron process. It seems the [U(IV)]/[U(III)] ratio in these molten salt mixtures can be controlled by the voltammetric method.
- Platinum, tungsten or molybdenum can be used as the material of the reference and working electrodes. If the electrodes are made of different materials, the thermal emf affects the results of potentiometric and voltammetric measurements.
- Next experiments will be done on BeF<sub>2</sub> containing systems.



**Thank you very much for attention.**