

On the Possibility of Quantitative Electrochemical Separation of Uranium from Gadolinium in Fluoride Melts

Martin Straka,^{1*} Lorant Szatmáry,¹ Martin Mareček,² Jan Uhlíř²

¹ ÚJV Řež, a.s., Hlavní 130, Husinec-Řež, CZ25068, Czech Republic, *Martin.Straka@ujv.cz

² Research Centre Řež, Hlavní 130, Husinec-Řež, Czech Republic, CZ25068

INTRODUCTION

The Molten Salt Reactor (MSR) is a non-classical (liquid fuel) system which can be operated as a breeder within the ²³²Th-²³³U fuel cycle with the very interesting breeding factor. The necessary precondition for its proper functionality is the on-line reprocessing within the MSR's fuel cycle. Therefore, a lot of effort is given to the development of the on-line pyrochemical reprocessing technology. Among the processes considered to be suitable for this process, the electrochemical separations are highlighted. Within this context, it is necessary to study electrochemical behavior of both fissile material and fission products in the molten salt systems and to develop the processes of their extraction from the system at various stages of the whole cycle. More details about MSR on-line reprocessing technology and also its connection to nonproliferation aspects can be found here.¹ In this contribution, continuation of the study of the electrochemical separation of U from Gd in the LiF-CaF₂ molten system by the modulated current electrolysis is presented.

Detailed knowledge of the electrochemical behavior of actinides and lanthanides in molten fluorides and of the processes involving these species is necessary to the development of any electrochemical separation process. If the fluoride carrier melt is electrochemically stable enough, it is possible to deposit the element of interest in its basic, metallic state by the electrolysis. In the case of insufficient electrochemical stability of the fluoride melt in which the actinides and lanthanides are dissolved for the experiments, it is possible to use a reactive working electrode made of a material which creates alloys with the element to be deposited. An alloying reaction can shift the deposition potential in a favorable direction and therefore achieve the separation of an element from the system. The use of reactive electrode can also improve the adhesion of the deposit. When two or more electroactive species are present in the system at the same time, the efficiency of their separation by an electrolysis depends on how different the deposition potentials of these two species are but if we input certain modulation to the electrolytic current, we can improve overall result of an electrolytic experiment. This method was used to separate uranium from gadolinium in LiF-CaF₂ melt.

EXPERIMENTAL

Within this work, a combination of a reactive electrode and a current modulation was used to separate uranium from gadolinium (representatives of fissile material and fission products) in the LiF-CaF₂ system.

All electrochemical experiments were carried out in the glassy carbon crucible placed in an electrolyzer made of INCONEL 625. The electrolyzer consists of a vessel closed by a removable flange with built-in holders for the electrodes, thermocouple and inlet and outlet of argon gas as described system is under an argon atmosphere (99.998 %) during the measurement. A resistance oven heats the electrolyzer and it provides homogenous thermal field up to 1,000°C. The whole apparatus is placed inside the glove box with dry nitrogen atmosphere (99.95 %). Typical content of moisture and oxygen in the glove-box is under 5 ppm for both water and oxygen. The three-electrode system was used for all measurements. Large surface glassy carbon crucible was used as a counter electrode. Nickel or tungsten wires were used as working electrodes. The potentials were referred to a 0.5 mm platinum wire immersed in the molten electrolyte, acting as a quasi-reference electrode. The electrodes were connected to HEKA PG 310 potentiostat (HEKA GmbH, Lambrecht, Germany) controlled by PC with the original software.

The melt used was a LiF-CaF₂ eutectic (79-21 mol%). Experiments in LiF-CaF₂ systems were done at 1,220 K. The current modulation used for electrolytic experiments was based on repeating pulses corresponding to parameters in TABLE I.

TABLE I. Structure of the current pulses used in electrolytic experiments. List the research results, and discuss the significance.

	Period			
	1	2	3	4
Current (mA)	-30	-10	10	0
Time (s)	1	10	2	1

The combination of SEM-EDX and ICP-MS analytical methods was used for evaluation the results.

RESULTS

The electrochemical behavior of uranium and gadolinium was measured in the LiF-CaF₂ system on Ni reactive working electrode. Both elements create intermetallic compounds with Ni which are clearly visible on cyclic voltammograms and chronopotentiograms (see Fig. 1).

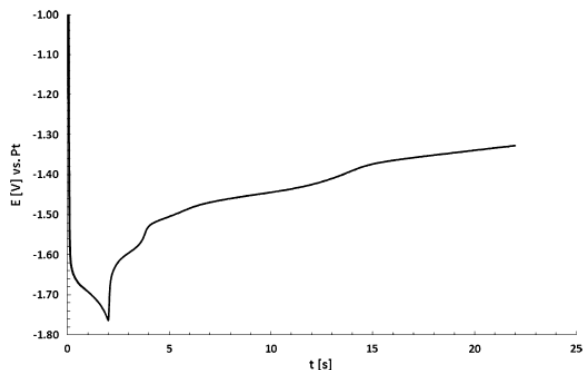


Fig. 1 Open-circuit chronopotentiogram of the LiF-CaF₂-GdF₃ system (3.4 wt%) at T = 1,223 K, Ni working electrode (0.08 cm²), Pt reference electrode

When both the uranium and gadolinium are present in the system, cyclic voltammogram shown in Fig. 2 was obtained. From the shape of the voltammogram, it can be expected that several Ni-U and Ni-Gd alloys are being deposited at certain potentials.

Resulting SEM micrograph can be seen in Fig. 3. Two clearly distinguished layers (depicted as „1“ and „2“ in the figure) were identified on the surface. Both these layers contain nickel and uranium in ratios 4.4:1 and 1.6:1 respectively. In both of these layers, only traces of gadolinium were detected

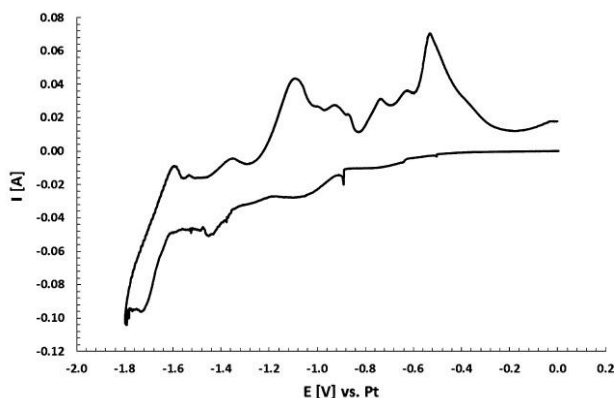


Fig. 2. The cyclic voltammogram measured in the LiF-CaF₂-UF₄-GdF₃ (3.5 wt.% for both U and Gd) system on Ni reactive electrode.

The effect of current modulation can be seen also in different amount of U and Gd in different distances from the electrode after the electrolysis. It can be seen in Fig. 4 that near the electrode (spot “1”), the amount of uranium is much higher than in higher distances (“spots “2” and “3”).

The uranium can be separated from gadolinium, the traces of Gd in the U-Ni deposit can probably be treated by the proper set-up of the electrolysis parameters. Therefore, the quantitative separation of uranium and gadolinium is probably achievable and it will be verified in the next group of experiments.

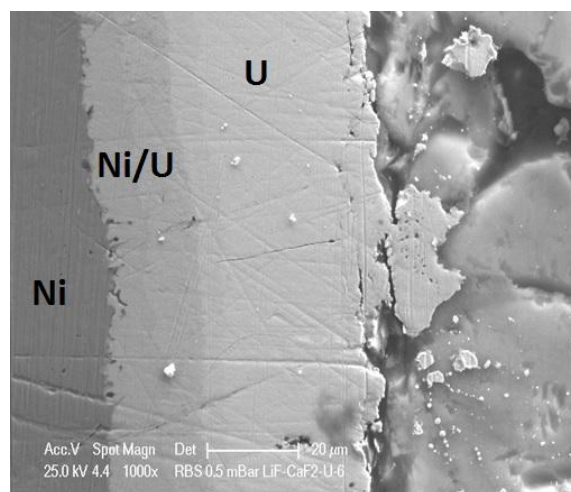


Fig. 3. SEM micrograph of the cross-section of a nickel wire after the electrolysis by modulated current in LiF-CaF₂-UF₄ (1.3 wt.%) system

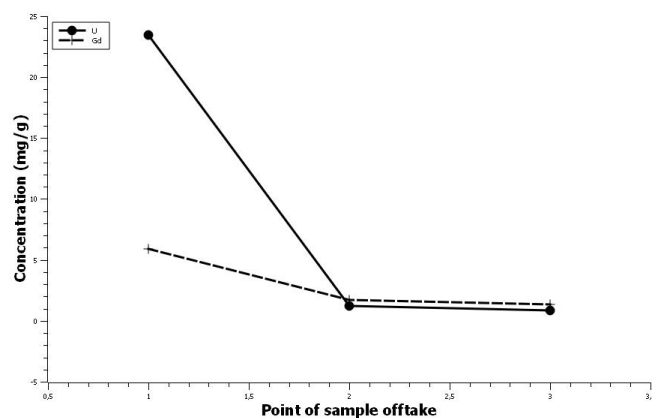


Fig. 4. Different amount of U and Gd in different distance from Ni WE after the electrolysis (“1” is nearest to WE, “3” is the most distance spot”)

REFERENCES

1. Uhlř J., "MSR On-line Reprocessing Technology and Nonproliferation Aspects," *Trans Am Nucl Soc.* **110**, 409-411 (2014).