Influence of conditions of Ag nanofoam electrodeposition on its performance in preparative debromination of aryl bromides

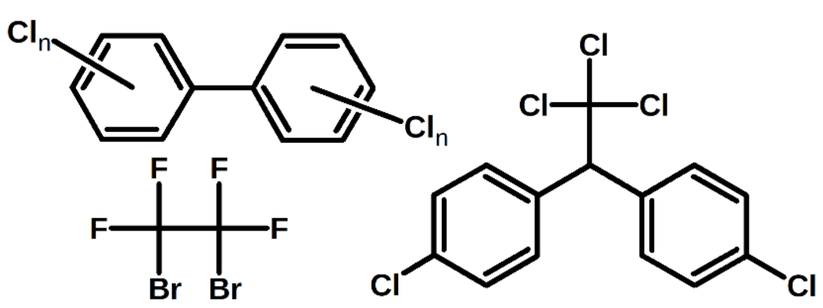
Lytvynenko A.S.[1], Tarasova I.V.[1,2], Gavrilenko K.S.[3], Kolotilov S.V.[1]

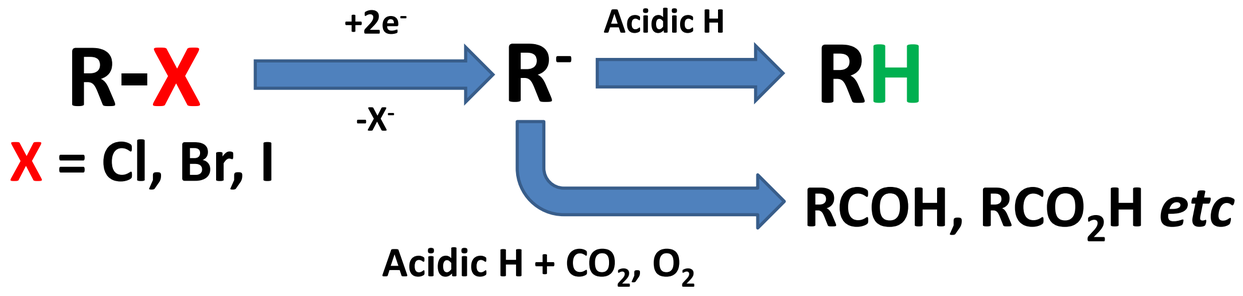
[1] Porous Compounds and Materials Dept., L. V. Pisarzhevskii Institute of Physical Chemistry of the NAS of Ukraine. Prospect Nauky, 31, Kyiv, 03028, Ukraine. E-mail: anton.s.lytvynenko@gmail.com

[2] Department of Inorganic Chemistry, Faculty of Chemistry, Taras Shevchenko National University of Kyiv. Lva Tolstogo str., 12, Kyiv, 01033, Ukraine

[3] ChemBioCenter, Taras Shevchenko National University of Kyiv, Chervonotkatska str., 61, 02094, Kyiv, Ukraine

- **Electrochemical reductive dehalogenation is a prospective tool for remediation of halogen-containing persistent organic pollutants, such as polyhalogenated biphenyls, freons, and inert pesticides [*Chem. Rev., 2016, 116, 15198–15234*].**

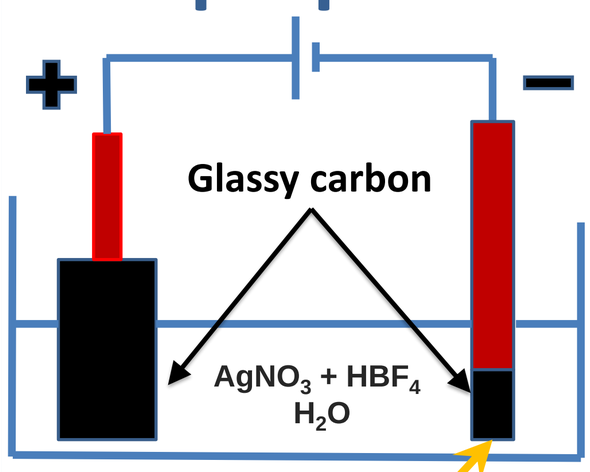




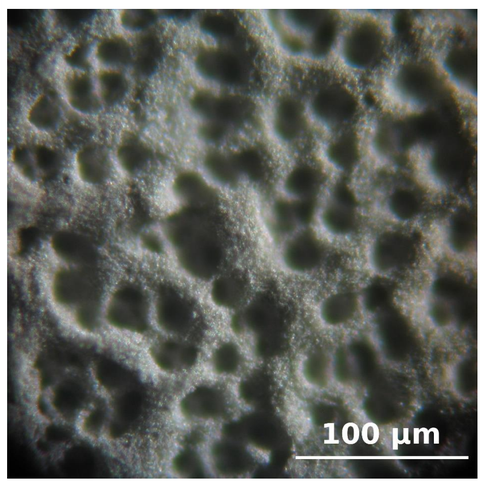
- **The process proceeds with high overpotentials, which justify the use of electrocatalysts.**
- **Silver cathode is one of the most efficient electrocatalysts of these reactions, its further nanostructuring can even improve the activity.**
- **High efficiency of silver nanofoams (NFs) as electrocatalysts of this process was previously shown by us *[New J. Chem., 2018, 42, 17499–17512]*.**

The aim of the work was to elucidate the influence of the electrodeposition conditions on the performance of the resulting Ag NF in electrochemical dehalogenation of 1-fluoro-4-bromobenzene (FPhBr).

NFs preparation



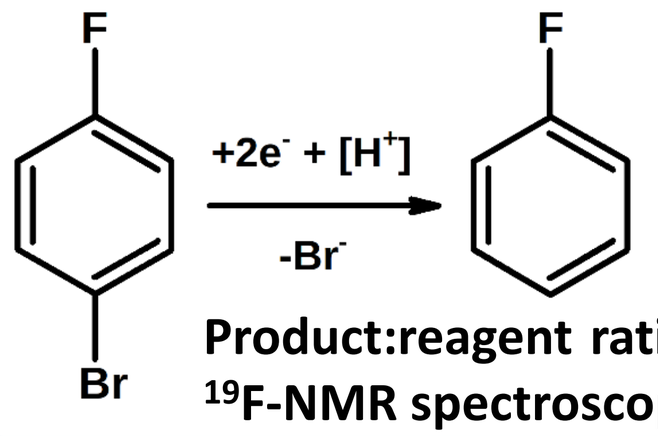
[H$^+$] = 1M.
[Ag$^+$] varied.
j = 3A/cm^2.
Time varied.



Assessment of the activity

Electrolysis of 1-fluoro-4-bromo-benzene in 3-electrode undivided cell with Mg sacrificial anode.

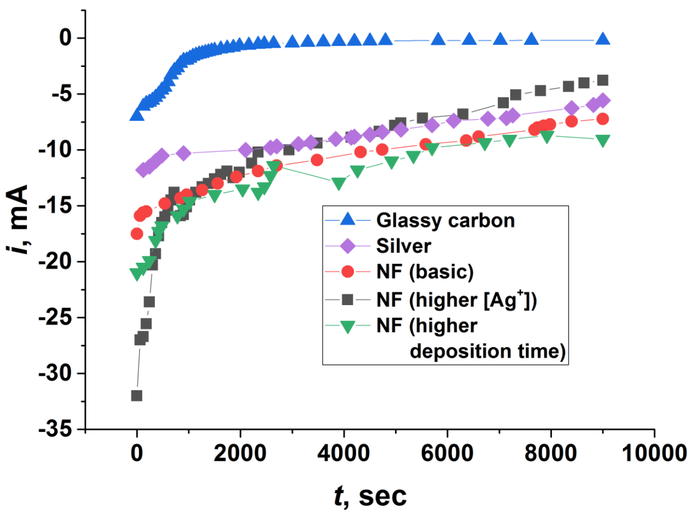
E = -2.4 V vs 0.1 M AgNO$_3$(CH$_3$CN)/Ag, *t* = 2.5 h. CH$_3$CN, inert atmosphere (Ar).

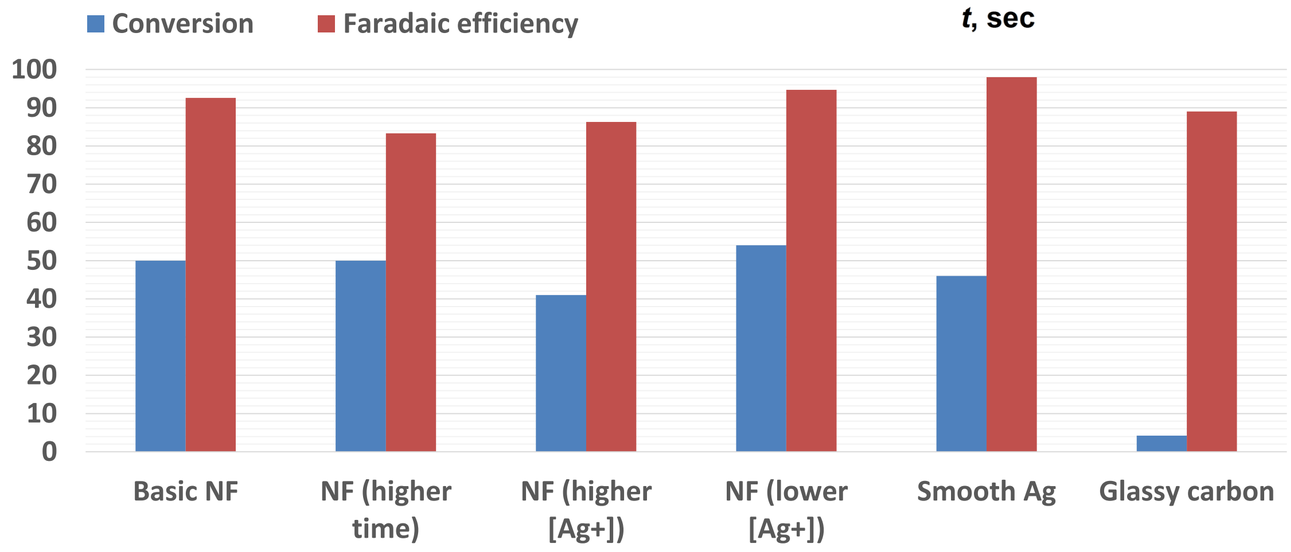


Product:reagent ratio quantified via ^{19}F-NMR spectroscopy.

The comparison of the NFs

- **Basic NF ([Ag+] = 0.01 M, 60 sec);**
- **NF deposited at higher time (120 sec);**
- **NF deposited from the bath with higher [Ag$^+$] (0.02 M);**
- **NF deposited from the bath with lower [Ag$^+$] (0.02 M);**





The experiments were performed in the conditions leading to the theoretical conversion ca. 40-60% (in order to facilitate the comparison)

1. **The decrease of [Ag$^+$] in the deposition bath led to increase of the resulting Ag nanofoam activity in reductive debromination of 1-fluoro-4-bromobenzene (both in the terms of conversion and Faradaic efficiency). The effect could be explained by decrease of Ag particles within the NF due to their slower growth at lower [Ag$^+$].**
2. **The increase of the deposition time led to lower Faradaic efficiency of the process on the resulting NF, which could be explained by higher size of the particles deposited at the longer time.**