

Anodic Partial Fluorination under Ultrasonication

Toshio Fuchigami, Takeshi Sunaga,
Hideki Ishii, and Mahito Atobe

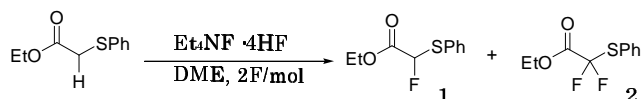
Department of Electronic Chemistry,
Tokyo Institute of Technology
Midori-ku, Yokohama 226-8502, Japan

Organofluorine compounds are highly useful in various fields such as material science, medicinal chemistry, and theoretical chemistry. As a novel synthetic method of organofluoro compounds, we have established electrochemical partial fluorination, which can be carried out without any hazardous reagents under mild conditions.^{1,2)} However, these electrochemical fluorinations are not always easy due to the low nucleophilicity of fluoride ions and anode passivation.

On the other hand, ultrasonic effects on electrochemical processes have received much interest, since the product yield and selectivity in the processes are greatly affected by promotion of mass transport caused by a cavitation micro-jet stream. Moreover, the micro-jet stream can also clean the electrode surface.

From the above viewpoint, effects of ultrasound on the anodic fluorination of ethyl α -phenylthioacetate in an organic solvent were examined in this work (Scheme 1). The yield and selectivity for the α -monofluorinated product **1** was greatly increased by ultrasonication as shown in Figs. 1 and 2. This ultrasonic effect could be rationalized in terms of mass-transport promotion of the substrate by the sonication.

Furthermore, we have also demonstrated that the ultrasonication greatly increased the yield and selectivity in anodic fluorination of 4-thiazolidinone derivatives in Et₃N-3HF ionic liquid.



Scheme 1

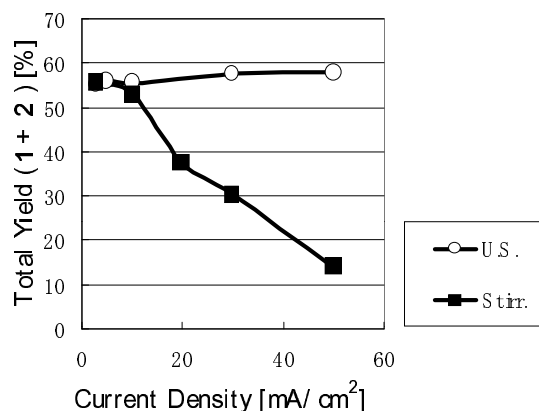


Fig. 1 Dependence of total yield (1+2) on the current density

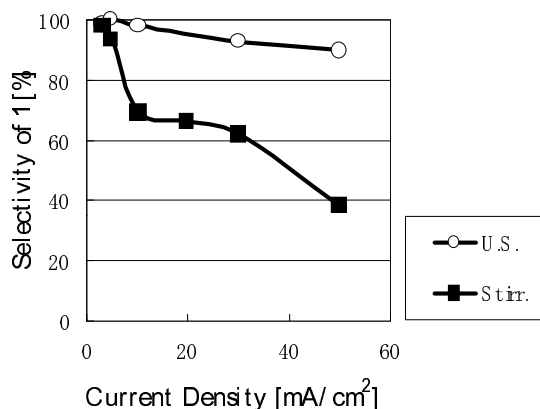


Fig. 2 Dependence of selectivity of 1 on the current density

References

- 1) T. Fuchigami, "Advances in Electron Transfer Chemistry, Vol. 6," P. S. Mariano ed., JAI Press, CT (1999), pp.41-130.
- 2) T. Fuchigami, "Organic Electrochemistry, 4th ed." H. Lund and O. Hamerich ed., Marcel Dekker, NY (2001), Chap. 25.