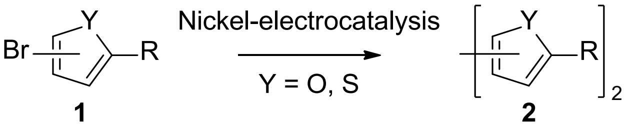
Nickel Electrocatalysed Synthesis of Bifurans and Bithiophenes

Valtteri Oksanen, Tom Wirtanen
Industrial Synthesis & Catalysis
VTT Technical Research Centre of Finland Ltd.
FI-02044 Espoo, Finland
email: tom.wirtanen@vtt.fi

Furan-based polymers have been in the recent years developed as an alternative for fossil-based materials. In this respect, the most advanced is the polyethylene furan-2,5-dicarboxylate (PEF) that has been envisioned as a replacement for polyethylene terephthalate (PET) [1]. Less research has been devoted to the synthesis and polymerization of bifurans [2]. These derivatives are readily obtained from hemicellulose-derived furfural, and they show some interesting complementary material properties [2a].

Nickel-electrocatalysed reductive homocoupling of (hetero)aryl (pseudo)halogens is a known methodology for the synthesis of the (hetero)biaryl moiety [3]. The described protocols typically employ a sacrificial anode which makes this method problematic from an environmental and economical point of view. Furthermore, the synthesis of bifuran and bithiophenes using this methodology is less well established compared to the biaryls and bipyridines.

We have recently developed reaction conditions for reductive nickel-electrocatalysis using carbon-based electrodes for converting several functionalized bromofurans and bromothiophenes to bifurans and bithiophenes [4]. Particularly, the reaction scope is examined from the point-of-view of potential applications for bio-polymer applications.



References

[1] A. Marshall, B. Jiang, R. M. Gauvin and C. M. Thomas, *Molecules*, **2022**, *27*, 4071.

[2] a) M. Ye, M. J. Kuo and R. F. Lobo, *Appl. Catal., A,* **2021**, *619*, 118138.; b) R. Wang, H. Zhang, M. Jiang, Z. Wang and G. Zhou, *Macromolecules*, **2022**, *55*, 190.; c) T. P. Kainulainen, T. A. O. Parviainen, J. A. Sirviö, L. J. R. McGeachie and J. P. Heiskanen *ACS Macro Lett.*, **2023**, *12*, 147.

[3] a) R. Rahll, S. Sengmany, E. L. Gall and E. Léonel, *Synthesis*, **2017**, *49*, 146.; b) K. W. R. de França, M. Navarro, É. Lèonel, M. Durandetti and J-Y. Nédélec, *J. Org. Chem.*, **2002**, *67*, 1838.; c) J. L. Oliveira, E. L. Gall, S. Sengmany, E. Léonel, P. Dubot, P. Cénédèse and M. Navarro, J. *Electrochim. Acta*., **2015**, *173*, 465.

[4] V. Oksanen and T. Wirtanen, *Manuscript in preparation*