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MOLECULAR ELECTROCHEMISTRY IN ORGANOMETALLIC SCIENCE

Book of Abstracts



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Organizers:

Jiří Ludvík (JHI FCH): jiri.ludvik@jh-inst.cas.cz
Irena Hoskovcová (ICT): Irena.Hoskovcova@vscht.cz
Ludmila Šimková (JHI FCH): ludmila.simkova@jh-inst.cas.cz
Radka Metelková (JHI FCH): radka@metelkova.cz
Věra Mansfeldová (JHI FCH): vera.mansfeldova@jh-inst.cas.cz

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Academy of Sciences of the Czech Republic
Dolejškova 3, 182 23 Praha 8, Czech Republic



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Synthesis and Electrochemical Studies of Rhenium(I) and Molybdenum(0) Complexes as Electrocatalysts for Reduction of Carbon Dioxide

Federico Franco, Cunfa Sun, Claudio Cometto, Roberto Gobetto, Carlo Nervi

Department of Chemistry, University of Turin, via P. Giuria 7, 10125, Turin, Italy,

e-mail: federico.franco@unito.it

The photochemical and electrochemical conversion of CO₂ to higher-energy products has been a focus of research as a path to renewable fuels. This thermodynamically unfavorable process can be improved by employing transition-metal coordination compounds which, in the form of molecular or supramolecular organometallic catalysts, are capable of mediating CO₂ reduction. Among them, we focused on Rhenium and Molybdenum. However, whereas a wide number of Rhenium(I) carbonyl-diimine complexes showed to be photo/redox active, and has already been successfully tested for the electrocatalytic CO₂ reduction, to our knowledge, there are no reports about the use of tetracarbonyl polypyridyl molybdenum(0) complexes as electrocatalysts for the reduction of CO₂. In this perspective, some [Mo(CO)₄(L)] (L= 2,2'-bipyridine (bpy); 1,10-phenantroline (phen) and similar derivatives) were synthesized and tested for electrochemical reduction of carbon dioxide. Moreover, a series of novel Re(I)-carbonyl diimine complexes has been synthesized and tested for the same purpose. The latter class of compounds is characterized by new polypyridyl ligands, derived from PNI-phen (N-(1,10-phenantroline)-4-(1-piperidinyl)naphthalene-1,8-dicarboximide), which revealed to be able to provide a 3000-fold excited state lifetime enhancement in a Re(I) charge-transfer complex [1]. The electrochemical behavior of both the classes of compounds was compared with the activity of Re(CO)₃Cl(bipy) [2].

Quite surprisingly, CV measurements (in MeCN and acetone), performed under both inert and CO₂ atmosphere at room temperature, revealed that [Mo(CO)₄(2,2'-bipyridyl)] shows redox activity as electrocatalyst for CO₂ reduction, although the overpotential at which the process occurs is rather negative (about -1.9 V vs SCE). The catalytic activity was also confirmed by controlled-potential electrolysis at -1.80 V, coupled with gas chromatography (GC).

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