

Alessia Fortunati PhD Thesis Summary

In such a historic moment of energy transition, which we are now experiencing, it is essential to evaluate and investigate new energy sources. It is of fundamental importance not only to use renewable energy as fuel but also to find an innovative use for waste materials such as carbon dioxide (CO₂). In a circular economy approach, this work deals with the electrocatalytic CO₂ transformation from waste material, harmful to the environment, to raw commodity for added-value chemicals and new future fuels. The European project SunCoChem fits into this scenario, and it has the purpose of developing a photoelectrochemical reactor capable of selectively capturing CO₂ from industrial fluegases and converting it into chemical materials useful for industry. This PhD thesis was mainly developed within the SunCoChem project, with the main aim of optimizing the electrocatalytic reduction of CO₂ in the presence of ionic liquids (ILs). Several imidazole-based ionic liquids were diluted in acetonitrile and then tested in two compartment (H-type) cell, using silver foil as working electrode. The ILs properties, as electrolytes, were evaluated by studying the conductivity and viscosity. An investigation of conductivity at low concentration was conducted to thoroughly understand the molar conductivity of each charge carrier within the solution composed of ILs and acetonitrile. The role of ILs in tuning the electrocatalytic CO₂ reduction reaction (CO₂RR) selectivity was investigated both from an experimental and a theoretical point of view. A correspondence between the nature of the anion of the ionic liquid and the selectivity was found. With fluorine-containing anions, carbon monoxide was selectively produced (F_{CO}>95%) while with acetate anions, under the same operating conditions, only hydrogen was generated as the gaseous product of the electrolytic reaction. Studies through density functional theory (DFT) and characterization techniques such as RAMAN and XPS lead to the rationalization of the formation of the carbene species, originated by the deprotonation of imidazole, which can impede the electrocatalytic reduction of CO₂ at the electrode. The inhibition can be caused either by the formation of the carboxylate or by the binding of the carbene to the electrode surface.

Once the best ionic liquid for the highly selective production of CO was found, the research focus was shifted on how to make the electrolytic system greener and more sustainable. In collaboration with Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, IPREM institute (Pau, France), polymeric ionic liquids (PILs) have been synthesized, in block and random configuration. Polymers based on styrene and vinylbenzyl chloride were functionalized with imidazole cation and then triflate and acetate anion were exchanged. Among these, polymers with triflate anion have been shown to be insoluble in water. By dip-coating technique, the PILs were deposited onto a silver surface and electrochemically tested in a single cell. The greenest procedure

improvement was to use a water-based electrolyte, instead of acetonitrile, thanks to the hydrophobicity of PILs with triflate. Another important aspect was the change in selectivity. With PILs deposited on Ag, in aqueous based electrolyte, interesting gaseous products such as carbon monoxide, methane and ethylene have been produced.

To conclude, until now interesting and promising results have been obtained by using ILs both as electrolytes ($FE_{CO} > 95\%$) and as polymers to coat a simple silver foil electrode (CH_4 , C_2H_4). For future developments, to deposit PILs on catalytic substrates different than silver, e.g., zinc, copper, should be investigated. The aim will be to optimize a more sustainable and less expensive electrolytic system for future electrocatalytic CO_2 conversion devices.