Lecture 11

Applications of N,N-bis(phosphonomethyl)glycine-derived Sn^{4+} or Co^{2+} phosphonates as proton conductors or energy-conversion electrocatalysts.

F. Cañamero-Cebrián[a], Rosario M.P. Colodrero[a], Álvaro Vilchez-Cózar[a], Montse Bazaga-García[a], Enrique R. Losilla[a], Pascual Olivera-Pastor[a], and Aurelio Cabeza[a]

[a]Universidad de Málaga, Dpto Química Inorgánica, Facultad de Ciencias, Campus de Teatinos s/n, 29071, Málaga, Spain

ernandocc@uma.es

Metal phosphonates (MPs), a subclass of coordination polymers, may exhibit acidic groups such as P-OH, SO_3H, COOH, N^+-H, etc. Combining these features with electrocatalytically active transition metals, make them highly appealing in the field of fuel cells and electrolysers, as potential proton conductors and/or precursors of electrocatalysts [1,2].

Herein, we investigate the synthesis, characterization and applications of a series of Co^{2+} and Sn^{4+} phosphonates derived from glycine-N,N-bis(methylenenphosphonic acid) (*BPMGLY*). In the case of the tin derivative, an amorphous compound, $Sn(C_4H_{11}O_8NP_2)_{0.75}Cl_{2.5}(H_2O)_{2.5}$ (Sn^{4+}- BPMGLY), was obtained by hydrothermal synthesis. Its pyrolytic treatment at 700 ºC in air led to an amorphous pyrophosphate, (Sn^{4+}-BPMGLY@700). Regarding cobalt phosphonates, three crystalline phases with composition $[Co(C_4H_9O_8NP_2(H_2O)_2]\cdot nH_2O$ (n=0, 2) were obtained and their crystal structure were solved. All families were extensively studied as proton conductors across a wide range of temperature and humidity conditions, displaying the Sn^{4+} derivatives the highest conductivity values of $7.99\cdot10^{-4}$ and $6.63\cdot10^{-3}$ $S\cdot cm^{-1}$ for Sn^{4+}-BPMGLY and Sn^{4+}-BPMGLY@700, respectively, at 95 °C and 95% relative humidity (RH) (Figure 1a). Furthermore, the cobalt phosphonates were utilized as precursors for non-precious metal catalysts (NPMCs), by pyrolysis in 5%-H_2/Ar at different temperatures and studied as electrocatalysts towards the oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) (Figure 1b).

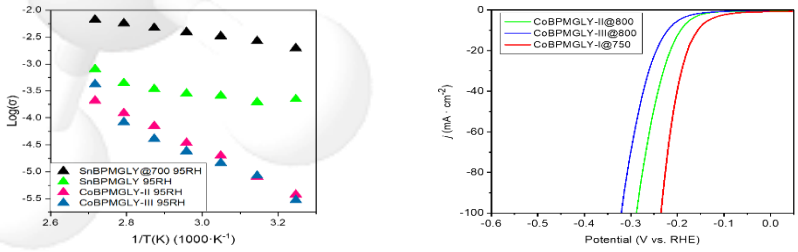

Figure 1. (a) Arrhenius plots of Sn^{4+}-BPMGLY, Sn^{4+}-BPMGLY@700, Co-BPMGLY-II and Co-BPMGLY- III at 95% RH. (b) HER LSV curves for pyrolyzed Co-BPMGLY derivatives.

References

1. Wu, J.; Wang, D.; Wan, S.; Liu, H.; Wang, C.; Wang, X. Small **2020**, 16, 1900550.
2. Zhang, R.; El-Rafaei, S.M.; Russo, P.A.; Pinna, N. J. Nanoparticle Res. **2018**, 20, 146.