DOI 10.5162/EUROSENSORSXXXVI/PT5.296

Metal-Organic Frameworks (MOFs)-Based Chemoresistive gas Sensors for Early Thermal Runaway Detection in Lithium-ion Batteries

Ignasi Fort-Grandas[1,2,3], Safa Aljemazi[2], Anna Estany-Macià[1,2], Yuzelfy Mendoza-Gamero[1,2,3], Paolo Pellegrino[1,2], Manel López[1,2], Christophe Serre[1,2], Arnald Grabulosa-Rodriguez[2,3], Mauricio Moreno-Sereno[1,2], Daniel Sainz[2,3], Anton Vidal-Ferran[2,3,4], Guillem Domènech-Gil[1,2], Albert Romano-Rodriguez[1,2,]*

[1] Department of Electronic and Biomedical Engineering, Universitat de Barcelona (UB), 08028 Barcelona, Spain

[2] Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona (UB), 08028 Barcelona, Spain

[3] Department of Inorganic and Organic Chemistry, Universitat de Barcelona (UB), 08028 Barcelona, Spain

[4]Catalan Institution of Research and Advanced Studies (ICREA), 08010 Barcelona, Spain

Corresponding Author's e-mail address: albert.romano@ub.edu

Summary:

Lithium-ion batteries (LiB) are used nowadays in a large number of applications, from electric vehicles to mobile phones and laptops, among others. The hazard of the operation of the LiBs is their thermal runaway, which can give rise to fire and explosion. Prior to these processes and while the battery is degrading, toxic and flammable gases are generated, whose detection could help in reducing the hazards. In this work, we synthesize conductive metal-organic frameworks (MOFs) and we prepare and we test them as room-temperature chemoresistive sensors for CO_2, CH_4 and H_2.

Keywords: chemoresistive gas sensors, metal-organic frameworks (MOFs), tryphenylene, lithium-ion batteries, thermal runaway

Background, Motivation and Objective

Lithium-ion batteries (LIBs) are used nowadays in a large number of applications, like electrical vehicles, laptops, mobile phones, … From the safety point of view, the major risk of LiB is their potential thermal runaway due to overcharging, internal/external short circuiting, and thermal failure, which can give rise to fire and explosion. During the initial stages of these runaway processes and before any reduction in the output voltage can be detected, the battery emits toxic and flammable gases, mainly CO_2 and H_2, but also CO, C_xH_y and VOCs [1]. Detecting these gases at an early stage could help in preventing the mentioned hazards.

Chemoresistive gas sensors based on metal oxides are known for more than 50 years and present high sensitivity to several gases, low cost, small size, easy operation and integration capabilities, but usually require high operating temperatures, making them not suitable for their integration into batteries. Promising results of chemoresistance at room temperature (RT) operation has been obtained with a specific family of metal-organic framework materials (MOFs), those based on triphenylene ligands [2,3]. In this work we will present the results of chemoresistive gas sensor fabrication and their response to several of the gases relevant in LiB degradation.

Methodology

For the formation of the MOF, hexahydroxytriphenylene (HHTP) has been used as the ligand and has been mixed with different metallic salts of cupper or nickel, following a modified route to the one described in [3]. The resulting black powder was collected by centrifugation, washed several times with distilled water and ethanol, and dried under nitrogen flow. These powders were structurally and chemically characterised to confirm the MOF formation and the crystalline nature.

For the fabrication of the resistive devices, the MOF powder was dispersed in water and drop casted onto either fused silica or oxidised silicon substrates containing interdigitated Cr/Au electrodes, which were fabricated using photolithography, metal deposition and lift-off processes. These devices were first electrically

characterised at room temperature to determine their I-V characteristics. The devices were next introduced in a self-designed gas tight chamber and were exposed to different pulses of the gases of interest, diluted in dry air, while their electrical resistance was monitored.

Results and discussion

The structural characterisation confirmed the crystalline nature of the MOFs, with typical pore size in the range of 1.9 to 2.1 nm, while the overall crystallite size is in the range of few to several hundreds of nanometres.

The chemoresistive sensing behaviour of these devices is demonstrated by exposing, e.g., to a pulse of 150 ppm of CO_2 diluted in dry air, as presented in Figure 1, showing a resistance increase of about 2%, while the baseline resistance is almost recovered after removal of the gas. This suggests some poisoning of the sensors during operation, which is consistent with the high absorption properties of this material, which is largely investigated for CO_2 capture [4].

The complete gas sensing response of the devices will be presented and discussed during the presentation. A critical discussion of the feasibility of these devices for early thermal runaway detection in LiB will be carried out.

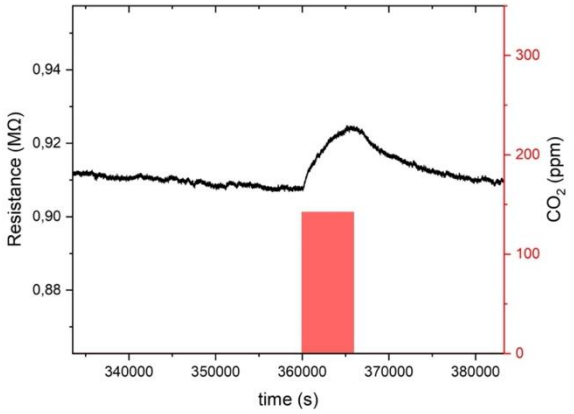

Fig. 1. Resistance variation of a $Cu_3(HHTP)_2$ MOF in the presence of 150 ppm of CO_2 diluted in dry synthetic air.

References

[1] C. Essl, L. Seifert, M. Rabe, A. Fuchs: Early detection of failing automotive batteries using gas sensors, *Batteries* 7, 25 (2021); doi: 10.3390/batteries

[2] W.T. Koo, J.S. Jang, I.D. Kim: Metal-Organic Frameworks for Chemiresistive Sensors, *Chem* 5, 1938-1963 (2019); doi: 10.1021/cr300014x

[3] M.G. Campbell, D. Sheberla, S.F. Liu, T.M. Swager, M. Dinca: Cu_3(hexaiminotriphenylene)$_2$: An electrically conductive 2D metal-organic framework for chemiresistive sensing, *Angewandte Chemie - International Edition* 54, 4349–4352 (2015); doi: 10.1002/anie.201411854.