Efficient Electrocaloric Cooling Through Polymer Nanocomposites with High Dielectric Strength

F. Le Goupil[1,2*], J. Martin[2], M. Valant[3], G. Hadziioannou[1] and N. Stingelin[2,4]
[1]Laboratoire de Chimie des Polymères Organiques (LCPO), Université de Bordeaux, CNRS UMR 5629, Allée Geoffroy Saint Hilaire, Bat. B8, CS 50023, 33615 Pessac Cedex, France
[2]Department of Materials, Imperial College London, Prince Consort Road, London SW7 2AZ, UK
[3]Materials Research Laboratory, University of Nova Gorica, Nova Gorica, 5000, Slovenia
[4]School of Materials Science and Engineering and School of Chemical and Biomolecular Engineering, Georgia Institute of Technology311 Ferst Drive, Atlanta, GA 30332, USA
*Florian Le Goupil: florian.le-goupil@u-bordeaux.fr

COP21 in Paris in 2015 led to 195 countries agreeing to collaborate to tackle climate change and restrict global warming to no more than 1.5°C. The refrigeration industry already contributes 10% of global carbon emissions, which has driven efforts towards the development of energy-efficient and environmentally friendly solid state cooling alternatives. Adiabatic depolarization cooling, which is based on the electrocaloric effect (ECE), has arisen as one of the main contenders. Lead-free relaxor ferroelectrics are suitable candidates for solid-state refrigeration, due to the extra contribution of their polar nano-regions (PNRs), however, their ECE must be increased. One approach is to operate close to critical points (CP) where energy barriers for switching between different phases are reduced, which leads to ECE enhancement, as we reported recently in doped-$(Na_{0.5}Bi_{0.5})TiO_3$ (NBT)[1,2] as well as Qian et al. in Zr-doped $BaTiO_3$(BT)[3]. However, very few reports of ECE>2K can be found for bulk materials due to the inability to apply sufficiently high fields to the ceramics.

Due to their active thicknesses of only few microns, multilayer capacitors (MLCs) significantly increase the electric field that can be applied, and the corresponding ECE, while keeping the applied voltage low. To that end we have produced and characterized the first multilayer capacitors of lead-free NBT-based materials. Good agreements with the corresponding bulk ceramics were found, including the position of characteristic temperatures such as the temperature of depolarisation and the “shoulder” temperature of the dielectric permittivity. Furthermore, values of ECE~2K were obtained. However, the potential of these MLCs for ECE applications was hindered by a systematic breakdown of the samples in the vicinity of 100kV/cm, due the low dielectric strength of doped-NBT, which needs to be significantly increased. A recent and highly promising approach to achieve this objective is to use polymer nanocomposite using high-ECE inorganic nanoparticles inside a ferroelectric polymer matrix.

We have produced nanoparticles of doped-$BaTiO_3$(BT) and doped-$(Na_{0.5}Bi_{0.5})TiO_3$ with diameters ~20-100nm by hydrothermal synthesis. Using different techniques, including drop-casting and spin-coating, we have shown that polymer nanocomposites with various thicknesses, using the well-known relaxor terpolymer PVDF-TrFE-CFE as matrix, can be produced. In addition to having a high ECE, the relaxor terpolymer shows a phase transition near that of the chosen inorganic nanoparticles, which is believed to lead to a further ECE enhancement. Moreover, electric fields >2500kV/cm were applied to the samples without breakdown and a significant improvement of permittivity and polarization was observed. Finally, direct ECE measurements using different techniques will be presented and the potential of this approach for efficient solid-state cooling will be demonstrated and discussed.

[1] F. Le Goupil, J. Bennett, A.-K. Axelsson, M. Valant, A. Berenov, A.J. Bell, T.P. Comyn, and N.M. Alford, Appl. Phys. Lett. **107**, (2015).
[2] F. Le Goupil, R. McKinnon, V. Koval, G. Viola, S. Dunn, A. Berenov, H. Yan, and N.M. Alford, Sci. Rep. **6**, 28251 (2016).
[3] X.-S. Qian, H.-J. Ye, Y.-T. Zhang, H. Gu, X. Li, C.A. Randall, and Q.M. Zhang, Adv. Funct. Mater. **24**, 1300 (2014).