

Operando in a transmission electron microscope characterization of two terminal devices

A/Prof Martial Duchamp^{1,2}

Dr Arnaud Demortiere^{3,4}, Miss Sorina Cretu^{1,2,3} and Miss Elizaveta Tiukalova^{1,2}

¹ Laboratory for in Situ & Operando Electron Nanoscopy, School of Materials Science and Engineering, Nanyang Technological University, Singapore, ² MajuLab, International Joint Research Unit UMI 3654, CNRS, Université Côte d'Azur, Sorbonne Université, National University of Singapore, Nanyang Technological University, Singapore, ³ Laboratoire de Recherche et Chimie des Solides (LRCS), UMR CNRS 7314, Amiens, France, ⁴ Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, Amiens, France

Due to high energy demand and intermittent electricity production of green energy, new devices architectures have been developed. In this contribution, we will present operando in a transmission electron microscope (TEM) characterizations of newly developed photo-voltaic devices based on organic-inorganic perovskite active layer, resistive switching memories based of SiO_x dielectric layer and all-solid-state batteries. These new devices architectures lead to new problems, mainly the stability over operation related to the creation of irreversible defects and micro-structural changes. The first approach used to tackle these problems from a micro-structural point-of-view is the use of post-mortem characterization techniques[1–3]. When a high spatial resolution is needed, the use of TEM allows in the same time to characterize the micro-structure and the composition. More recently, the need to understand the degradation mechanism as they are happening at atomic scale and the parallel development of MEMS-based in situ capabilities inside a TEM made possible the observation at atomic scale of the degradation mechanism of devices operando in a TEM[4–6].

The challenging part for operando in a TEM characterizations is the device preparation. We have previously demonstrated the approach consisting on fabricating a micro-sized solar cell on a MEMS chip[3]. More recently, an organic-inorganic MAPbI₃ perovskite solar cell was operated inside a TEM. In forward bias, Pb and I migrates at the hole transport layer, when in reversed biased, the overall perovskite layer get degraded and leads to the creation of PbI₂ nanoparticles and voids at the electron transport layer/perovskite interface[4]. We have applied the same methodology to all-solid-state batteries to determine and locate the degradation mechanism happening under operation inside a TEM. We found a careful control of the total electron beam dose is needed to prevent degradation from the electron beam. For this knowledge, we have been able to cycle the battery inside the TEM and determine the species involved in the degradation mechanism using a combination of TEM and spectroscopic techniques.

1. Qing, J. *et al.* Aligned and Graded Type-II Ruddlesden–Popper Perovskite Films for Efficient Solar Cells. *Adv. Energy Mater.* 8, 1800185 (2018).
2. Xu, W. *et al.* Rational molecular passivation for high-performance perovskite light-emitting diodes. *Nat. Photonics* 1 (2019). doi:10.1038/s41566-019-0390-x
3. Sun, S. *et al.* The origin of high efficiency in low-temperature solution-processable bilayer organometal halide hybrid solar cells. *Energy Environ. Sci.* 7, 399–407 (2013).
4. Duchamp, M. *et al.* Focused ion beam specimen preparation for electron holography of electrically biased thin film solar cells. in *Microscopy Conference MC2013, Regensburg, Germany, 25-30 August 2013* (ed. Rachel, R.) 242–243 (2013).
5. Duchamp, M. *et al.* In situ transmission electron microscopy of resistive switching in thin silicon oxide layers. *Resolut. Discov.* 1, 27–33 (2016).
6. Jeangros, Q. *et al.* In Situ TEM Analysis of Organic–Inorganic Metal-Halide Perovskite Solar Cells under Electrical Bias. *Nano Lett.* 16, 7013–7018 (2016).