

Tri-layer graphene as membrane and electrode for liquid-phase electron microscopy studies of CO₂ electroreduction nanocatalysts

[Saltanat Toleukhanova](#)¹, Dr. Tzu-Hsien Shen¹, Mr Chen Chang¹, Miss. Swathilakshmi Swathilakshmi¹, Miss. Tecla Bottinelli Montandon¹, Prof. Vasiliki Tileli¹

¹Institute of Materials, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Electrochemical liquid-phase electron microscopy (ec-LPEM) has been successfully applied to understand catalyst degradation during CO₂ electroreduction (CO₂ER).[1] However, to be able to fully reproduce full cell conditions at these highly cathodic potentials, further advances in imaging and electrode configuration are required. Herein, we have integrated tri-layer graphene to serve as a liquid-sealing membrane and a substrate electrode material and tested its applicability for studying nanocatalysts at realistic CO₂ER potentials.[2]

All experiments were carried out in a dedicated scanning electron microscopy (SEM) stage that is equipped with bulk reference and counter electrodes. The fabrication of the working electrode started by patterning a single Pt electrical pad on a Si/SiN_x electrochemical chip with an electron transparent window. Holes were perforated onto the 50 nm thick SiN_x membrane in a cleanroom. Tri-layer graphene was obtained via PMMA-assisted wet transfer of monolayer graphene sheets. The final tri-layer graphene was wet transferred on the electrochemical chip, ensuring the coverage of the electrical contact and membrane area. To assemble the graphene electrochemical microcell, the graphene chips were treated with H₂ plasma to ensure their hydrophilicity. Subsequently, Cu nanocubes (NCs) were drop-casted on the graphene region overlapping with the perforated SiN_x support membrane.

First, we evaluated the inert potential range and stability of the graphene cells and the results showed that the graphene electrode has a wider inert potential range in the cathodic region than the conventionally used glassy carbon electrode. Graphene was also found to have a stable current profile for up to 10 min at a cathodic potential of -1.1 V vs RHE, which is common for bulk cell CO₂ER studies. In addition, cyclic voltammetry tests with Cu₂O NCs loaded on graphene allowed for the investigation of Cu oxide reduction and oxidation peaks, confirming a good charge transfer between graphene and catalyst. Overall, the bench-top experiments demonstrate the suitability of graphene as a substrate electrode for CO₂ER studies. Furthermore, in situ SEM control experiments showed improved spatial resolution with the graphene membrane and also demonstrated reduced electron beam induced damage in the bare graphene region compared to the SiN_x region. However, in situ SEM electrochemical tests indicated the presence of adverse synergistic effects of e-beam and applied cathodic potential on the electrochemical stability time window of graphene electrodes. These effects are shown to be mitigated by minimizing the electron beam dose (i.e. probe current) or avoiding high cathodic potentials. Optimized in situ SEM experiments on Cu NCs, performed at -1.1 V vs RHE, a probe current of 16 pA and a duration of 3 min, revealed that their degradation proceeds via a subtle dissolution and redeposition mechanism during CO₂ER.

In conclusion, this work demonstrates that graphene can play the dual role of membrane and electrode for investigating the degradation mechanisms of CO₂ER catalysts under realistic potentials, while increasing the spatial resolution for ec-LPEM studies.

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CO₂_electroreduction, Cu_nanocubes, liquid-phase_electron_microscopy, graphene, microcells

Reference:

- [1] J. Vavra, T. Shen, D. Stoian, V. Tileli, R. Buonsanti, *Angew. Chem. Int. Ed.* 2021, 60, 1347.
- [2] S. Toleukhanova, T.-H. Shen, C. Chang, S. Swathilakshmi, T. Bottinelli Montandon, V. Tileli, *Adv. Mater. n.d.*, n/a, 2311133.