

Measurement of Li-Ion Self-Diffusion in Laser Structured Electrodes

Sacris Jeru Tambio¹, Michael Deschamps², and Wilhelm Pfleging¹

¹ Karlsruhe Institute of Technology, Institute for Applied Materials, Germany

² Universite d'Orleans, France

It is generally stated that a limiting factor in fast charging and high-power discharging of lithium-ion batteries (LiB) stems from the diffusion kinetics of Li^+ in the electrode pore network. Numerous approaches in enabling fast charging of LiBs include active material development, electrolytes with high ionic conductivity and the management of the charging and discharging temperature. Another promising method is laser micro structuring to modify the electrode architecture regarding an enhanced lithium-ion diffusion kinetics. An increased high-rate capability and boost in cell lifetime have been demonstrated with such 3D electrodes [1, 2] but the related mechanisms leading to a substantial impact to diffusion kinetics are still poorly understood. Furthermore, it is imperative to find an optimal ablation pattern with regard to the desired application scenario that minimizes active mass loss in order to create the economic basis for efficient upscaling of the process.

Nuclear Magnetic Resonance (NMR) measurements of longitudinal (T_1) and transverse relaxation times (T_2), as well as the T_2/T_2 exchange, are routinely used for the identification of different molecular species. The exchange NMR experiment is a well-known technique for studying local environments of nuclei such as liquids in pores and approximating their shapes and sizes [3]. The evolution of the transverse relaxation rate (T_2) of a probed nuclei allows to determine if the specie is confined (shorter T_2) or in liquid bulk (longer T_2). In this work, so-called Exchange Nuclear Magnetic Resonance (T_2/T_2 exchange or EXSY), is conceptualized to study the impact of laser generated 3D patterns in pore self-diffusion of electrolyte species.

Exchange NMR and T_1 and T_2 measurements were realized at various soaking times and electrolyte amounts for the following electrolyte species: Li^+ , PF_6^- , ethyl carbonate (EC), and ethyl methyl carbonate (EMC), using laser structured, graphite-based electrodes casted on non-metallic substrates (to reduce RF interference). 2D exchange maps show the presence of confined species as well as the approximation of the diffusion properties. Using isotope exchange experiments with ^6Li enriched electrolyte, concentration maps revealed the rate of $^6\text{LiPF}_6$ intrusion into $^7\text{LiPF}_6$ rich pre-soaked electrodes. The impact of laser generated 3D patterns in pore diffusion will be discussed in detail.

- [1] Zheng, Y. et al. 3D silicon/graphite composite electrodes for high-energy lithium-ion batteries. *Electrochim. Acta* 317, 502–508 (2019).
- [2] Smyrek, P., Pröll, J., Rakebrandt, J.-H., Seifert, H. J. & Pfleging, W. Manufacturing of advanced $\text{Li}(\text{NiMnCo})\text{O}_2$ electrodes for lithium-ion batteries . *Laser-based Micro- Nanoprocessing IX9351*, 93511D (2015).
- [3] Mitchell, J. et al. Validation of NMR relaxation exchange time measurements in porous media. *J. Chem. Phys.* 127, (2007).