Doctoral Dissertation
Doctoral Program in Material Science and Technology (37th Cycle)

Ceramic materials for energy storage and conversion devices

Synthesis, processing and recycling

By

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Politecnico di Torino

2025

Abstract

This PhD thesis addresses key challenges in the field of energy materials, focusing on two critical areas: the development of NASICON-type glass-ceramic solid electrolytes for next-generation solid-state batteries (SSBs), and the selective recovery of ceramic components from end-of-life (EoL) solid oxide cells (SOCs) to support a circular economy in hydrogen technologies. The work was carried out within the framework of the Si-DRIVE and BEST4Hy European projects, respectively.

Chapter 2 explores the melt-casting synthesis and optimization of Li-ion conducting glass-ceramics based on $Li_{1.4}Al_{0.4}Ge_{0.2}Ti_{1.4}(PO_4)_3$ (LAGTP) and $Li_{1.5}Al_{0.3}Mg_{0.1}Ge_{1.6}(PO_4)_3$ (LAMGP). The Ti-rich LAGTP system was investigated to combine the good glass-forming ability of LAGP with the high conductivity of LATP. Among the routes explored, melt-cast bulk samples outperformed sintered counterparts due to a more favorable microstructure with larger voids and improved grain cohesion. Doping with B_2O_3 significantly enhanced conductivity and reduced activation energy by promoting grain boundary cohesion growth, and inhibiting microcrack formation. In contrast, LAMGP-based systems showed excellent glass-forming ability, allowing the fabrication of amorphous systems. Among various oxide additives tested, B_2O_3 proved most effective in enhancing conductivity without inducing detrimental secondary phases. Both LAGTPB and LAMGPB systems demonstrated high anodic stability (>4.8 V vs Li^+/Li), making them suitable for high-voltage cathodes. The chapter provides key insights into how composition and processing affect structure and performance in NASICON-type electrolytes.

Chapter 3 investigates the use of ultra-fast high-temperature sintering (UHS) as an alternative to conventional sintering, addressing key limitations such as long durations, energy intensity, and lithium volatilization. The study compares B_2O_3-modified LAMGPB with a commercial LAGP reference. UHS enabled rapid densification and crystallization into a pure, conductive LAGP phase in both systems. The tailored LAMGPB composition showed superior structural integrity and densification, improved grain cohesion and growth, and reduced grain boundary resistance which resulted in higher total ionic conductivities. These findings underscore the relevance of tailoring glass-ceramic compositions to fully benefit from UHS and provide a route toward scalable, fast and energy-efficient processing of solid electrolytes for SSBs.

Chapter 4 shifts focus to the circularity of SOCs by developing a scalable recycling process for NiO and YSZ, in both separate and composite forms. A laboratory-scale workflow was optimized, combining 6 h of milling, hydrothermal treatment (HT) at 200 °C, and selective Ni leaching using diluted HNO_3. HT enabled effective disaggregation of the composite Ni-YZ powders, while preserving YSZ structure and enabling the recovery of high-purity NiO via oxalate precipitation. The process was scaled up to TRL 5 using a 2 L hydrothermal reactor. Optimized conditions (temperature, acid concentration, solid:liquid ratio, time) allowed recovery of high-quality YSZ with low Ni residues (0.1-0.3 wt%). Treating entire EoL cells eliminated unscalable steps like mechanical polishing and sieving, and enabled ~90 wt% yield for both YSZ and NiO. Recovered YSZ showed similar ionic conductivity and microstructural features to virgin 3YSZ, supporting its reuse in fuel support layers. Eventually, the direct recovery of NiO-YSZ composites from both scrap and re-oxidized EoL SOCs proved viable, with 30 wt% recycled material used in the fuel electrode supports of newly manufactured cells, that performed comparably to standard ones. Further optimization is needed to improve mechanical strength for stack assembly.

Overall, this thesis demonstrates how advanced ceramic design, fast processing, and material recovery strategies can contribute to greener energy technologies. It offers a foundation for scalable

implementation of solid-state batteries and SOC circularity, while identifying open challenges such as batch variability, milling optimization, and structural control—key directions for future research and industrial application.