Abstract

The last decades are characterized by the rapid spread of technological innovation, which demands an ever-increasing number of devices and systems accompanied by low-power sensor networks. In this framework, the production of cost-effective solutions with minimal environmental impact or disposal issues, which guarantee a long operational lifetime, and with a solid safety setpoint to prevent leakages, flammability and pollution represents a key challenge. In this context, this thesis focuses on the development of composite gel polymer electrolytes (GPE) as safe alternatives to liquid electrolytes for electrochemical devices. The liquid electrolyte substitution significantly reduces leakage, evaporation, and flammability risks while potentially extending device lifetime. The GPEs were tested both in harvesting (dye-sensitized solar cells, DSSCs) and storage (hybrid lithium-ion capacitors, LICs) technologies, then successfully integrated. The exploitation of the same GPE matrix structure, adapting only the charge carriers, enables the possibility of facile integration of the two technologies to develop autonomous harvesting-storage systems for maintenance-free IoT sensors, with strong potential for industrial production. The main objective was to investigate the behaviour of a gel polymer electrolyte based on polyvinylidene fluoride-co-hexafluoropropylene-co-acrylic acid (PVDF-HFP-AA) prepared through low-impact, one-pot processes in acetone without thermal treatments, yielding self-standing composite membranes retaining ~70 wt% liquid electrolyte. Different mechanical reinforcement strategies are investigated by introducing silica fillers, studying how morphology, particle size, and specific surface area affect dispersion within the composite, as well as by employing a bifunctional organosilane. This coupling agent may enhance compatibility between the organic PVDF-HFP-AA polymer and inorganic silica phases. The most promising formulations are implemented in a LIC, replacing liquid electrolyte with the GPE delivering specific energies ~10-15 Wh/Kg (C/10), energetic efficiencies ~80% over 40 cycles, and low self-discharge compared to supercapacitors. The GPE was also tested in DSSCs, reaching power conversion efficiencies ~3% under 1 sun and up to ~12% under 1000 lux, with stable performance in flexible configurations. After optimization at device level, these two technologies are finally coupled to realize a self-powered, low-energy system suitable for sensor applications, achieving PV efficiencies ~7% (1000 lux), storage efficiencies >50% and overall harvesting-storage efficiencies ~5%, with the storage unit demonstrating negligible self-discharge and tolerance to fluctuating photocurrent, all enabled by sharing the same quasi-solid electrolyte architecture.