Innovative electrode chemistry in ionic liquid electrolytes for sodium-less battery systems

Gianni APPETECCHI - *Sapienza University of Rome*

Sodium as well as lithium metal anodes are affected by severe passivation phenomena by the electrolyte, leading to unwelcome surface growth up of passive layers and/or dendrites which deplete the performance and safety of the electrochemical device. Silica-gel based electrode substrates (SGESs), able of hosting sodium within their porouos structure, were proposed in the place of conventional Na° metal anodes because of their capability of allowing very homogeneous sodium plating, thus remarkably reducing dendritic formation. Therefore, SGESs were addressed to sodium-less battery systems where the Na° anode is initially missing.

In this work, the behaviour of SGESs was investigated in innovative electrolytes based on salts molten at room temperature, called ionic liquids (ILs). ILs, highly retardant fluids with negligible vapor pressure, are proposed as alternative solvents to volatile and hazardous alkyl carbonates, commonly used in sodium batteries, for enhancing the safety and reliability level of the electrochemical device.

The SGESs were prepared by blending the active material (Sodium silica-gel) with the electronic conductor (carbon) and a polymer binder (PEO or PVdF). Trimethyl-butyl-ammonium bis(fluorosulfonyl)imide ($N_{1114}FSI$), synthesized and purified in our labs, was selected as the ionic liquid in combination with the NaTFSI and NaFSI salts. XRD, Raman and SEM-EDX analysis were carried on SGESs for investigating their chemical structure whereas galvanostatic cycling tests were run to examine the electrochemical performance. Tests in organic electrolyte were carried out for comparison purpose.

The data show a coulombic efficiency equal to 100 % starting from the 1st cycle and for more than 500 cycles in conjunction with very low cell voltage (3-30 mV), highlighting for efficient and reversible Na° stripping/plating process. These results are likely ascribable to an optimal electrode/electrolyte interphase due to the good film-forming ability of the FSI anion. SEM-EDX analysis, carried out after prolonged cycling tests (> 500 cycles), evidences stronger degradation for the FSI anion with respect to the TFSI one and a thicker passive film in the PVdF-containing SGESs. The $N_{1114}FSI$ ionic liquid shows a better compatibility with SGESs and Na° electrodes with respect to the organic solvents. The best performances were found in the NaFSI-based electrolyte.

To summarize, this work demonstrated the feasibility of ionic-liquid electrolytes in sodium-less batteries, enhancing the safety/reliability and, at the same time, the electrochemical performance (as compared with organic electrolytes).