Fundamental understanding of concentrated aqueous electrolytes for batteries by radiolysis

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Aqueous electrolytes, studied since the 1990s, are a way to solve the current problems of Li-ion batteries in terms of safety, cost and environmental impact. However, their energy density is limited by the narrow thermodynamic stability window of water (1.23 V). The concept of concentrated aqueous electrolytes has completely changed this vision with the discovery of the so-called water-in-salt electrolyte (WISE), obtained by dissolving a large amount of salt in water. These electrolytes can be depicted as few water molecules surrounded by cations and anions forming ion pairs. This change of solvation structure compared to classical electrolytes (salt solvated by water) increases the stability window. Nevertheless, there is no comprehensive view of concentrated aqueous electrolytes and fundamental questions remain [1]. To what extent is water limiting the stability window, how does the increase in molality affect the organization in solution, or what is its influence on reaction mechanisms are all paths to explore. In this presentation, we will focus on lithium (bistrifluoromethanesulfonyl(amide) (LiTFSI) salt, whose solubility in water at room temperature can be as high as 21 $mol.kg^{-1}$.

Studying these electrolytes by radiolysis provides an accelerated chemical approach [2] to get a deeper understanding of the reactions at stake and assess the viability of these electrolyte solutions. The degradation process with radiolysis studied with the ALIENOR platform is much shorter than the electrochemical one and mimics the products of salt and solvent degradation observed during long battery operation [3]. Radiolysis also allows studying these solutions at very different timescales. Thus, picosecond pulse radiolysis experiments carried out on the ELYSE platform of the Institut de Chimie Physique (Université Paris Saclay) were performed and allowed monitoring the behavior of the hydrated electron in solutions of different molalities. Lastly, the identification of stable products formed in the liquid and in the gas phase at different molalities enabled us to propose reaction mechanisms in these WISEs under solicitation [4]. A new cell, enabling to perform electrochemical and radiolysis experiments, will also be presented.

References

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