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Competition between electronic attachment and solvation revealed thanks to radiolysis

Sophie Le Caër

NIMBE, UMR 3685 CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France; Email: sophie.le-caer@cea.fr

A convenient way to generate charges (electrons and holes) in materials and to study their fate consists in using ionizing radiation.¹ Indeed, ionizing radiation penetrates in the depth of the material, generating charge carriers. During this presentation, we will focus on the behavior of electrons. Once generated, they can either solvate or attach to the molecule(s) of interest. We will illustrate this competition between both processes by two recent examples and show how this affects subsequent reactions.

The first one is imogolite nanotubes. Two types of inorganic aluminosilicate nanotubes are studied: one is hydrophilic on its external and internal surfaces (IMO-OH) while the second has a hydrophobic internal cavity due to Si-CH₃ bonds (IMO-CH₃), the external surface remaining hydrophilic. Picosecond pulse radiolysis experiments evidence that the electrons are efficiently driven outward. For samples with very few external water molecules (around 1% of the total mass), quasi-free electrons are formed. They can attach to a water molecule, generating the water radical anion, which ultimately leads to dihydrogen. When more external water molecules are present, solvated electrons, precursor of dihydrogen, are formed. The attachment of the quasi-free electron to water is a very efficient process and accounts for the high H₂ production at low relative humidities values. When the water content increases, the solvation of the electron is preferred. These latter species lead to H₂ production, but in a lower extent than quasi-free electrons.

The second one is fluoroethylene carbonate (FEC). We have investigated the degradation mechanisms induced by irradiation in FEC, a cyclic carbonate, which is an additive commonly used in lithium-ion batteries. Picosecond pulse radiolysis experiments performed in neat FEC evidence that the FEC^{•-} radical anion is directly formed by attachment of the quasi-free electron to FEC, the solvation of the electron being a minor channel. The same observation was also performed in propylene carbonate, a cyclic carbonate. This behavior is due to a high affinity of the solvent for the electron.² However, when FEC is a solute and not the solvent, the FEC^{•-} species is not observed. This latter species is no longer stabilized by the solvent, and linear radical anions are formed after ring cleavage. Reaction mechanisms are proposed to account for the formation of the various gases detected, which are mainly CO and CO₂.

References

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