

Effect of Particles Sizes on Electronic Structure of Nanooxides and Character of Interatomic Bonds Formation in Composites at Mechanical Activation and Pyrogenic Synthesis

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Energy redistribution of valence electrons during dispersion of solids to nanosizes is a result of differences in splitting of energy levels of atoms in volume and atoms with broken bonds on the nanoparticles surface. Number of these bonds is commensurate. Such redistribution depends on atomic-crystal structure, chemical bonding and charge state of ions. The energy distribution of electrons gets narrow simultaneously with increasing density in a high-energy region at the top of valence band in crystals with significant bonds covalence while these bonds break and binding states dehybridize.

Relaxation processes in highly disordered crystals and amorphous phases leads to a shift of the energy distribution towards low energies due to absence of strictly directed dehybridized orbitals and their overlapping.

The energy distribution gets narrow in oxides with high-charged anions, where electrons transferred from cations occupy non-binding high-energy electronic states, occurs due to return of electrons to cations when bonds breaking during dispersion.

Mechanical activation of single-component nanooxides leads to narrowing of energy distribution of electrons due to particles dispersion. Mechanical activation of two-component mixtures of nanooxides results in significant widening of superposition of the Op -electrons energy distribution towards low energies, where Op_{π} -binding states concentrate.

Analysis of the OK_{α} , SiL_{α} and AlL_{α} ultra-soft X-ray emission bands of alumina-silica nanocomposites, corresponding to the energy distribution of the Op -, $Sisd$ - and $Alsd$ -valence electrons showed that low-energy widening of the Op -electrons distribution is a consequence of splitting of Op -energy levels during π -overlapping of p -orbitals of oxygen surface atoms in SiO_2 and Al_2O_3 nanoparticles in the process of mechanical activation due to high local pressures and temperatures.

Decreasing occupation of the high-energy $Sisd$ - and $Alsd$ -levels indicates that split Op_{π} -levels were occupied by electrons transferred from silicon and aluminum cations. Therefore, oxygen charge in binding states significantly increased as a result of mechanical activation. This effect caused an increase of the charge capacity of lithium power supplies made of alumina-silica nanocomposites. Charge capacity increased during cycling. It is possible since increased oxygen ions charge increases number of Li^+ ions intercalated into structural channels of material and lithium ions can not tear electrons from

binding levels off in order to recombine to neutral atoms. Therefore, they go out from cathode and together with ions from anode increase number of charge carriers during the next cycle under deintercalation. Li^+ ions easily tear electrons from non-binding states in non-activated mixtures and recombine to free atoms, which are extremely active and oxidize creating LiO film that disable deintercalation and counteract the cycling.

Bonds between the surface atoms of nanoparticles during pyrogenic synthesis form with formation of SiO_2 layer on the Al_2O_3 particle. It was confirmed by half decreasing intensity of the AlL_α as compared to that of the SiL_α versus spectra obtained from mechanical and mechanically activated nanocomposites.