How to measure the oxygen coefficient in complex oxides

October 12 2016

Scientists of the Faculty of Chemistry of the Lomonosov Moscow State University under the leadership of Prof. Yury Teterin and in cooperation with Russian and British colleagues have developed a technique to evaluate the oxygen coefficient of uranium in complex oxides. Information about the uranium oxidation state, the oxygen coefficient in complex uranium oxides UO2+x, and their ionic composition (U4+, U5+, U6+) has great scientific and economic value.

UO2+x is a generalized formula of all complex uranium oxides reflecting the fact that uranium in this substance could have simultaneously several oxidation states. The oxygen coefficient determines stoichiometry of complex uranium oxide, showing the proportion of oxygen atoms to single uranium atoms in the chemical formula.

Oxygen coefficient determination is necessary for multiple technologies: development of uranium deposits; preparation of nuclear reactor fuel; prognostication of processes that accompany uranium fission in reactors; establishing radioactive nuclear waste disposal templates; and the development of technologies used for environmental rehabilitation from radioactive nuclear waste.

Researchers used X-ray photoelectron spectroscopy (XPS) and different X-ray diffraction methods. XPS is the most effective method for determining the uranium oxidation state, along with other chemical elements of actinide series. This method is based on the photo effect and receives pulses from electrons from different atom energy levels. For instance, the U 4f line in the spectrum means that there's an electron of the f-orbit, which is located on the fourth in succession (counting from the core) electronic shell.

Scientists have proved that correct value of the oxygen coefficient in UO2+x can't be obtained with information about values of the U 4f peak intensities and the O 1s electrons of core levels. So with the new technique, scientists have applied peak intensity of the outer U5f electrons for quantitative evaluation of the oxygen coefficient.

"Our technique rests on the results of wide experimental and theoretical research of the nature of chemical bound in uranium oxides. It's physically based and obtains the most correct results," says Professor Yury Teterin.

X-ray photoelectron spectroscopy (XPS) was used to study both polycrystalline and non-crystalline samples of uranium oxides. In order to get XPS reference spectra, scientists have exploited monocrystalline films of separate uranium oxides. Such spectra are necessary for comparison with corresponding theoretical spectra and also for examination of radiation damage to samples. Obtaining such films is a problem, which was solved in the published work in cooperation with foreign collaborators.

"It was established that 129Xe23+ xenon ion irradiation of monocrystalline films results in significant violation of long- and short-range order in the structure and an increase of the uranium oxidation state. The same processes occur in a nuclear reactor. The obtained results are proven by X-ray diffraction analysis data, which was also used in our research," says Yury Teterin.

While studying the influence of uranium and argon ion irradiation on

UO_2 monocrystalline films, it was found that on the uranium oxide surface, a stable phase of uranium oxide is formed, $UO_{2.12}$. Its oxygen coefficient is 2.12. The composition of this phase in broad range doesn't depend on irradiation intensity and temperature of sample annealing. This trend would be developed in further researches.

The fundamental scientific task of the study is the determination of the oxidation state, ion composition and the nature of chemical bound of actinide compounds on the basis of XPS fine structure parameters, their core and outer electrons.

It has applications in all stages of nuclear power generation, from uranium ore production and finishing to transmutation of spent fuel. The research could contribute to radioactive nuclear waste disposal templates and also could be applicable for development of technologies for environmental rehabilitation after accidents involving radioactivity.

More information: Yury A. Teterin et al, XPS Study of Ion Irradiated and Unirradiated UOThin Films, *Inorganic Chemistry* (2016). DOI: 10.1021/acs.inorgchem.6b01184

Provided by Lomonosov Moscow State University