Spectroscopic analysis of solid oxide fuel cell material with XPS

Author
Paul Mack
Thermo Fisher Scientific
East Grinstead, West Sussex, UK

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The surface of solid oxide fuel cell was studied with Thermo Scientific™ Nexsa™ XPS System. The elemental and chemical composition of the surface was investigated to determine the performance of the material under thermal cycling.
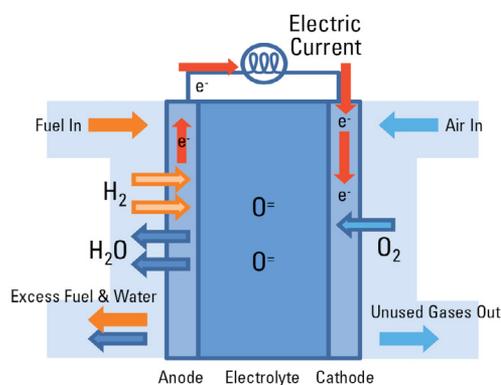
Introduction
Solid oxide fuel cells are electrochemical devices which convert a fuel directly into electricity. They are characterized by high efficiency, low emissions and long term stability. The fuel cell device consists of porous cathodic and anodic layers with a dense, solid oxide electrolyte between them (Figure 1). The purpose of the cathodic layer is to reductively ionize atmospheric oxygen and transport it through to the electrolyte, where it meets the fuel. The overall efficiency of the device is related to the cathode's ability to promote this so-called Oxygen Reduction Reaction. One of the materials of interest as fuel cell cathode layers is strontium-substituted lanthanum cobaltites. With these perovskite materials, the catalytic activity is affected by the elemental composition and chemistry of the surface. The chemical specificity of XPS makes it the ideal technique for analysing solid oxide fuel cells.

Thermo Scientific Nexsa XPS System

Experimental
XPS was used to study a candidate cathode material before and after annealing in air at high temperature, simulating the thermal cycling of a real solid oxide fuel cell device. A lanthanum strontium cobaltite (LSC) layer was analysed before and after annealing at high temperature. This layer was deposited onto an yttrium-stabilized zirconia (YSZ) substrate with a gadolinium-doped ceria barrier layer between them. The LSC layer acts as a cathode while the YSZ is the dense electrolyte (Figure 2). The top surface of the LSC was analysed non-destructively with XPS to obtain chemical and elemental information of the surface of cathode layer. The rate at which oxygen is absorbed from the air and converted into ions depends on the chemistry and composition of the outermost surface of the LSC.
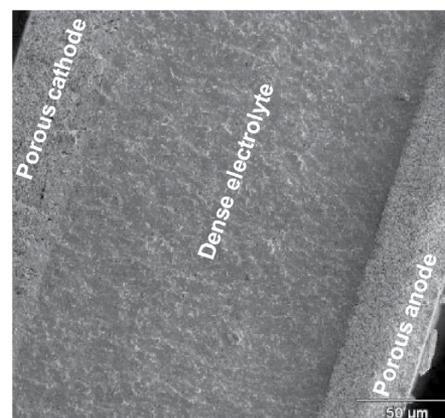

Figure 1: Schematic of operation of solid oxide fuel cell

Figure 2: Scanning Electron Microscope image of cross section of solid oxide fuel cell

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Results

A straightforward, non-destructive XPS analysis of the top surface of the LSC layer revealed significant changes in the film composition caused by annealing. In Figure 3 is the comparison of the elemental compositions of annealed and as received samples. In both the as received and annealed films, the cobalt concentration is significantly less than the expected value. Also the ratio of lanthanum to strontium is not optimal in either case. Additionally, because the ratio changes between the as received and unannealed cases, it indicates that the film is not stable under thermal cycling conditions which may be experienced while in use.

$$La/Sr_{as\ rec} = 2.8$$
$$La/Sr_{annealed} = 4.3$$
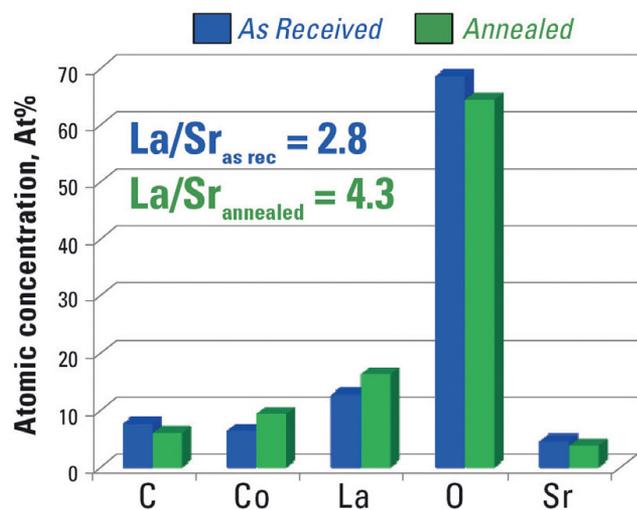
Top Surface Atomic Concentration At%

Element	Expected	As Received	Annealed
(La+Sr)	20.00	17.32	20.10
Co	20.00	6.38	9.42
O	60.00	68.63	64.49
La/Sr	–	2.8	4.3

Figure 3: Elemental quantification of surface composition of annealed and as received samples

High energy resolution XPS analysis of the carbon spectrum (Figure 4a) from the LSC top surface enables identification of the carbon bonding states present. Observed *C-C* and *C-O* components are from adventitiously-deposited carbon, typically found on any sample that has been in the atmosphere for any substantial period of time. At the higher binding energies the components are due to inorganic carbonates. There is less carbonate on the annealed surface, and the difference in carbonate peak width may indicate that the carbonate in the annealed sample forms on a more physically ordered surface. The assignment of a carbonate component in the carbon spectrum is confirmed with the strontium high resolution spectrum. The strontium spectrum from the as received sample shows two bonding states. These can be assigned to strontium carbonate and strontium in the LSC lattice. Interaction between the orbital and spin angular momentum of ionized strontium results in two XPS peak components for each bonding state. Annealing in air at high temperature has significantly decreased the amount of strontium carbonate relative to the concentration of lattice- bound strontium atoms. These carbonates have a detrimental effect on the oxygen reduction reaction at the top surface and hinder the oxygen ion transport through the LSC layer. As a result, the overall performance of the solid oxide fuel cell would be adversely affected.

The chemistry of lanthanum at the top of the LSC surface can be monitored using a very simple metric (Figure 5). Strong electron orbital-spin angular momentum interactions cause a splitting of lanthanum XPS peaks. The magnitude of this splitting and the ratio of the split components is diagnostic of the chemical states present. Lanthanum oxide and carbonate, for example, have splittings which are different by 1 eV. On the as received surface, the splitting is as expected for carbonate, in accord with the carbon and strontium data already shown. After annealing, the splitting increases towards the value for lanthanum oxide, indicating that the level of carbonate has dropped but still is not pure lanthanum oxide bonding. Instead, the data are consistent with a mixture of oxide and carbonate.
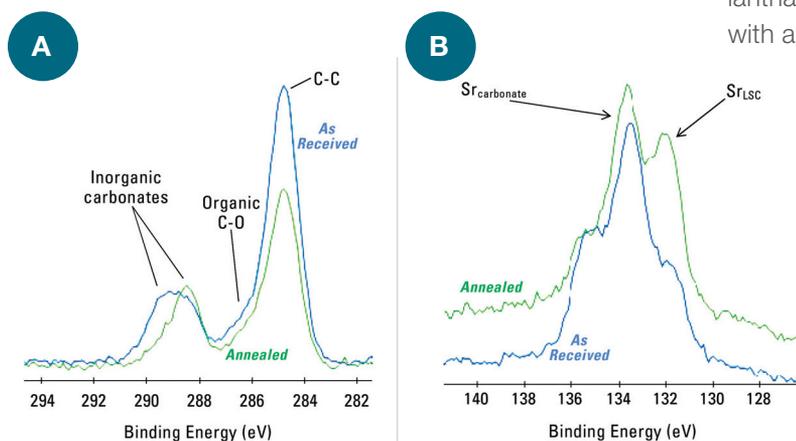

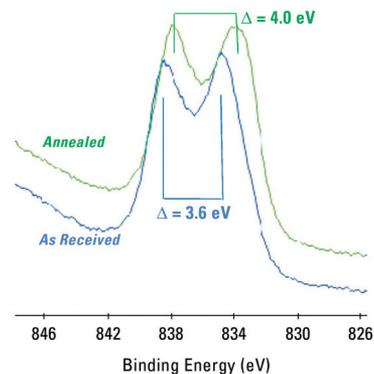Figure 4: High resolution spectra of a) carbon and b) strontium

Figure 5: High resolution lanthanum spectra of the surface

Using the non-destructive technique of angle resolved XPS analysis it is possible to find out about the depth distribution of strontium carbonate in the top few nanometers of the LSC layer. The information depth of XPS changes when collecting electrons from different photoemission angles. With strontium using photoemission angle normal to the sample surface the information depth is 0 to 6 nm into the surface. When using a shallow angle, a much thinner layer of the surface, between 0 and 3 nm, is sampled. It can be seen in Figure 6 that the relative proportions of strontium in the LSC lattice and carbonate states changes significantly, with the carbonate relatively stronger when sampling only the top 3 nm which confirms that the carbonate is a surface species.

Cobalt chemistry at the top surface of the LSC layer was investigated using two methods, looking at the core and valence levels of cobalt atoms. In Figure 7a the broad band between 0 and 6 eV is due to hybridization of O2p and Co3d valence orbitals. The narrow band at 2.2 eV has previously been assigned to transition metals in a +3 oxidation state in a polyhedral arrangement with oxygen. After annealing, this band increases in intensity, indicating that the concentration of Co(III) at the LSC top surface increases with annealing. Valence band analysis has shown us that there is Co(III) on the LSC surface. High energy resolution XPS analysis of the cobalt core levels in Figure 7b, however, indicates that we also have Co(II). In LaCoO3, with no strontium atoms, we would expect to see only Co(III), but substitution of strontium into the lattice at the expense of lanthanum increases the number of oxygen vacancies, resulting in the formation of cobalt +2 oxidation state. The ratio of the XPS satellite peaks, which are diagnostic of Co(II), to the main peak can be used to quantify the cobalt +2 and +3 oxidation states. We can see that in agreement with the valence band analysis, the XPS core-level data show the amount of Co(III) in the LSC top surface increases on annealing in air.
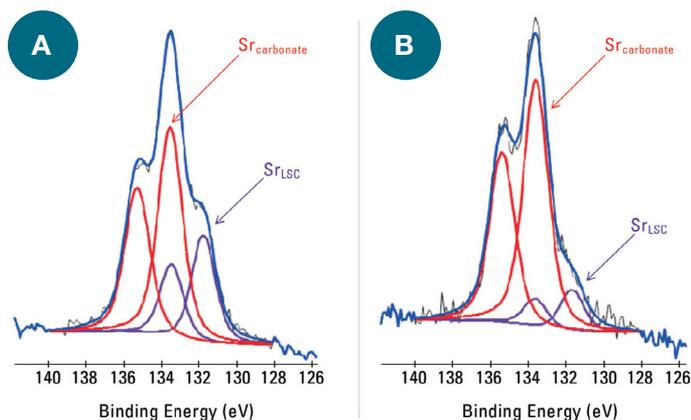

Figure 6: High resolution strontium spectra of the as received sample a) normal photoemission angle and b) shallow photoemission angle
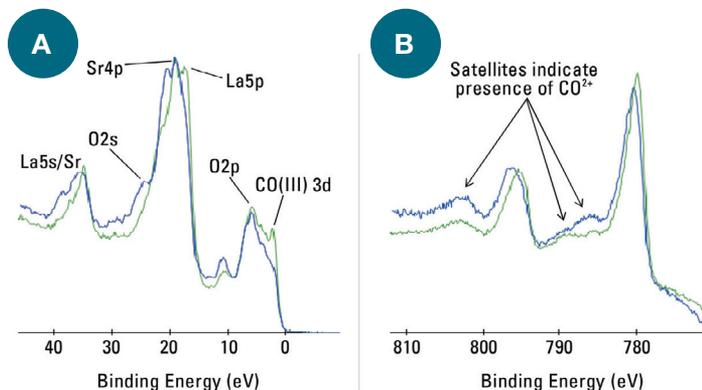

Figure 7: a) Valence band spectra and b) High resolution cobalt spectra from as received and annealed LSC surfaces (0-6 nm)

Summary

Potential solid oxide fuel cell material was studied with Nexsa. A lanthanum strontium cobaltite (LSC) layer was analysed before and after annealing at high temperature to simulate the thermal cycling of a real solid oxide fuel cell device. It was found that the amount of carbonate on the surface reduces during annealing. These carbonates have a detrimental effect on the oxygen reduction reaction at the surface and hinder the oxygen ion transport through the LSC layer. It was also found that the carbonates are located to the first 3 nm of the surface. This kind of information can be only obtained with XPS because of its unique surface sensitivity and chemical specificity.

Acknowledgements

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