

Surface analytical methods for the development of electrochemical components of polymer electrolyte fuel cells

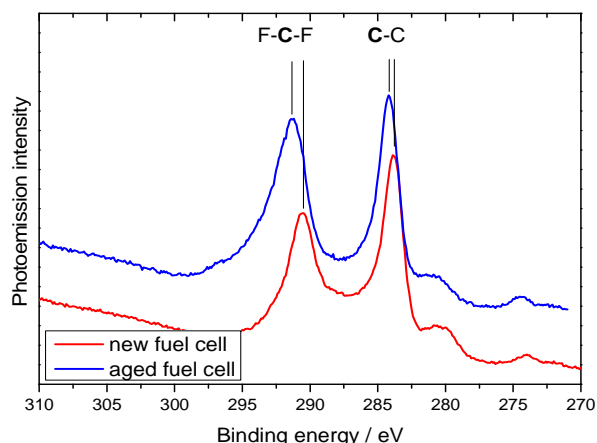
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The transition from fossil to renewable energies implies significant changes in the energy system regarding the distribution, storage and energy conversion due to the intrinsic natural fluctuations of renewable power sources. Polymer electrolyte fuel cells (PEFC) are highly efficient electrochemical energy converters that may be implemented in a wide range of power and dynamics. Their high gravimetric energy density makes them attractive for many applications, especially for mobile purposes. In particular they are a key to hydrogen fuelled electric cars.

However, improving the durability of fuel cells is still an important issue. The understanding of the occurring degradation mechanisms is a crucial step in the development of sustainable fuel cells with long operational times.

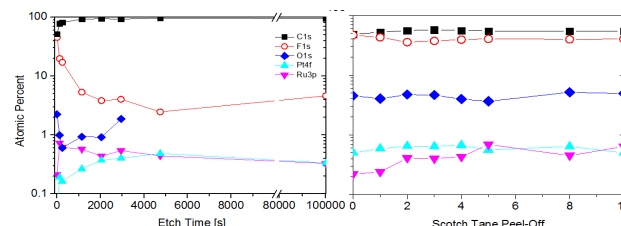
Surface analytical methods provide insight into the surface chemistry of PEFCs and allow the studying of degradation products and mechanisms. The combination of methods gives complementary information about the investigated fuel cell components. X-ray photoemission spectroscopy (XPS) yields information about elements and binding states.



C1s photoemission spectra of catalyst layers with two components (carbon support: 284.5 eV; PTFE: 291 eV): signal ratio is reduced and binding energy is shifted due to ageing.

One of the outstanding aspects of photoemission spectroscopy is the extremely high surface sensitivity in the nanometer range. In combination with an ablative technology this allows for depth profiling, exploring the chemistry of deeper layers, where compounds, e.g. catalysts may be depleted by segregating to the surface. For ablative investigations are necessarily combined with a partial destruction of the samples it is crucial to ensure the investigated chemistry is not modified during the process, or the modifications can be understood. A common technology is etching the surface with a defocused or scanned beam of high energy argon or oxygen ions, typically. In the case of PEM fuel cell components such argon “sputtering” treatment has shown to be disrupting the polymer structure and thus not feasible for depth profiling. Another, rather low tech approach is more successful: stripping off a common office style adhesive tape removes a layer of 2-4 μm of the sample material. Sequential “peel-off” and

photoemission experiments yield reasonable depth profiles of elemental distribution.

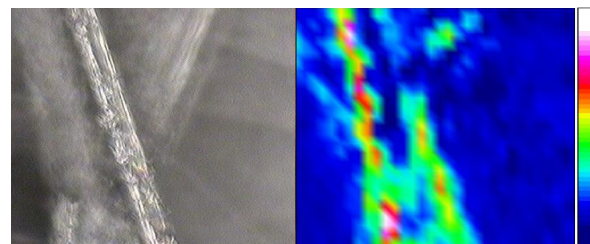


Comparison of different types of depth profiles of a catalyst layer

Left: Conventional Ar^+ ion etching with a typical saturation profile due to ion beam induced decomposition
Right: Peel-off depth profile (given in peeling steps) showing a Ruthenium depletion at the surface

Infrared and Raman spectromicroscopy in combination with scanning and/or imaging techniques allows a fast investigation of larger sample areas. This approach is complementary to the detailed photoemission studies. Due to roughness and reflectivity issues the use of diffuse reflection or attenuated total reflection in direct contact (ATR) need to be pondered.

An overview of the applied surface analysis methods and their advantages and difficulties is presented.



Optical and IR image of a gas diffusion layer of a PEFC, focusing on a surface fiber. A high PTFE content (bright colors) is to be seen at the edge and in the gaps between carbon fibers.

References:

- [1] M. Schulze, N. Wagner, T. Kaz, K. A. Friedrich, *Electrochim. Acta* 2007, 52, 2328.
- [2] M. Schulze, K. Bolwin, E. Gülzow, and W. Schnurnberger, *Fresenius J. Anal. Chem.* **353**, 778 (1995).
- [3] Y. Chung, et al., *J. Phys. Chem. C*, **2008**, 112, 313.