For direct ethanol fuel cells (DEFCs) to become viable, the efficient oxidation of ethanol at the anode is required, such that all twelve of the possible electrons are captured in converting the chemical energy of the ethanol molecule. Carbon supported Pt can work (1), but tends to become poisoned by intermediate reaction products (2). It is therefore necessary to develop multifunctional catalysts with reduced Pt content (1-3). One possible solution is to combine Pt with Sn which overcome these limitations (1-3). Reactivity measurements show favourable trends with Pt-Sn bimetallic catalysts (2, 3). Pt-Sn can form a variety of different phases, which are usually cubic or hexagonal, but in general, only the Pt3Sn (cubic) and PtSn (hexagonal) are reported in fuel cell catalysts (4).

From a TEM point of view, distinguishing the different Pt-Sn phases is challenging because the spatial frequencies (and atomic plane spacings) of Pt-Sn bimetallic phases are similar to Pt (4). We use a mixture of HRTEM, HAADF-STEM and electron diffraction techniques to investigate the nanostructures of fresh Pt3Sn/C and PtSn/C electrode catalysts supplied by Johnson Matthey.

Figure 1 shows HAADF-STEM images of a Pt3Sn/C and PtSn/C catalyst. The nanoparticles are on average approximately 4 nm in diameter on the Pt3Sn/C catalyst and appear to be separate crystals. By contrast, nanoparticles on the PtSn/C catalyst form an almost continuous layer of metal on the surface of the carbon support. The nanoparticles on the PtSn/C catalyst are approximately 2 nm diameter on average. Figure 2 shows higher magnification HAADF-STEM images. Clusters were observed in both electrode catalysts. Intensity variations in the nanoparticles such as the central nanoparticle in Figure 2(b) could be explained by the random occupation of Sn within the Pt lattice since HAADF-STEM is sensitive to atomic number. Figure 3 shows HRTEM images of the two electrode catalysts, which show clearly the difference in nanoparticle morphologies between the two catalysts. Measuring the lattice spacings from most of the nanoparticles suggests Pt or Pt3Sn in the Pt3Sn/C catalyst, in addition to some SnO2 crystals. A wider range of lattice spacings in the PtSn/C catalyst were measured suggesting the presence of different Pt-Sn phases and SnO2.

References

Acknowledgement: The authors thank the EPSRC for support from critical mass EPSRC grant EP/J018058/1
Fig. 1: HAADF-STEM images of the (a) Pt3Sn/C and (b) PtSn/C electrode catalysts.

Fig. 2: High magnification HAADF-STEM images of the (a) Pt3Sn/C and (b) PtSn/C electrode catalysts.

Fig. 3: HRTEM images of the (a) Pt3Sn/C and (b) PtSn/C electrode catalysts.