

Introduction

Mixed metal electrodes containing two or more metals have shown to have a significant increase in overvoltage towards hydrogen evolution and long-time stability compared to bare single metal electrodes. Of specific interest are electrodes containing silver doped with one or more metals (e.g. mercury, bismuth, copper and gold) [1-3]. Changes in the surface chemistry can be explained from changes in the electronic structure of the surface, resulting in modifications in the adsorption energies and barriers for the reactions. This effect may be local to an alloying atom, or it may be of longer range. Further, the introduction of different species into a surface creates chemically different sites on the surface. This provides a range of different sites for e.g. adsorption, and hence will also change the distribution of transition states available for reaction or dissociation.

The increasing overvoltage towards HER could therefore be explained from a decrease in the total coverage of adsorbed hydrogen on the electrode surface or due to changes in the activation energies for the HER. In the case of AgBi mixed metals this effect can be considered as a result of the spontaneous enrichment of the surface metal layer by the surface active component (Bi) of the alloy [4] as Ag being the surface-active component in the Ag-Au alloys [3]. The same process could also be explained by change in the rate of surface oxidation and thus the long-time stability. The observed changes in surface oxidation could be explained by changes in oxidation incubation time, oxide nucleation rate, oxide growth kinetics, and nucleation activation energy for alloyed metals due to segregated bismuth to the topmost layer.

Preliminary results

The ionic structures of AgBi mixed metal surfaces have preliminary been characterised using Surface X-ray Absorption Fine Structure (SEXAFS). Data have been recorded at Bi L_{III} (13.419 keV) and Ag K (25.514 keV) edges. Polished and oxidised AgBi surfaces with different Bi content (AgBi0.8, AgBi6 and AgBi20) have been studied. Preliminary SEXAFS results shown by comparison of radial distribution functions as fingerprints of the different oxidised samples indicate:

-Bi-Bi distances at 3.2 Å are removed for polished samples (Figure 1). Result is consistent with formation of Bi₂O₃ (Bi_{II}-Bi_{II} of 3.28 Å reported in the literature [5]).

-Increasing the Bi is consistent with introducing more Bi-Bi (3.2 Å) distances in oxidised samples (Figure 2). The distance is not present in the AgBi0.8 sample.

For the AgBi alloy with less Bi content (AgBi0.8) no distances typically for Bi₂O₃ [4] are present. Whereas Bi_I-Bi_I at 3.9 Å seen which may indicate formation of BiO on the surface of oxidised samples. For the AgBi6 and AgBi20 alloys the Bi-Bi of 3.2 Å indicates formation of Bi₂O₃ on surfaces. The result of this is increased long-time stability for these surfaces, by introducing Bi₂O₃ which is a conductive oxide. Future work will of course include a fully structural study by using least squares algorithms.

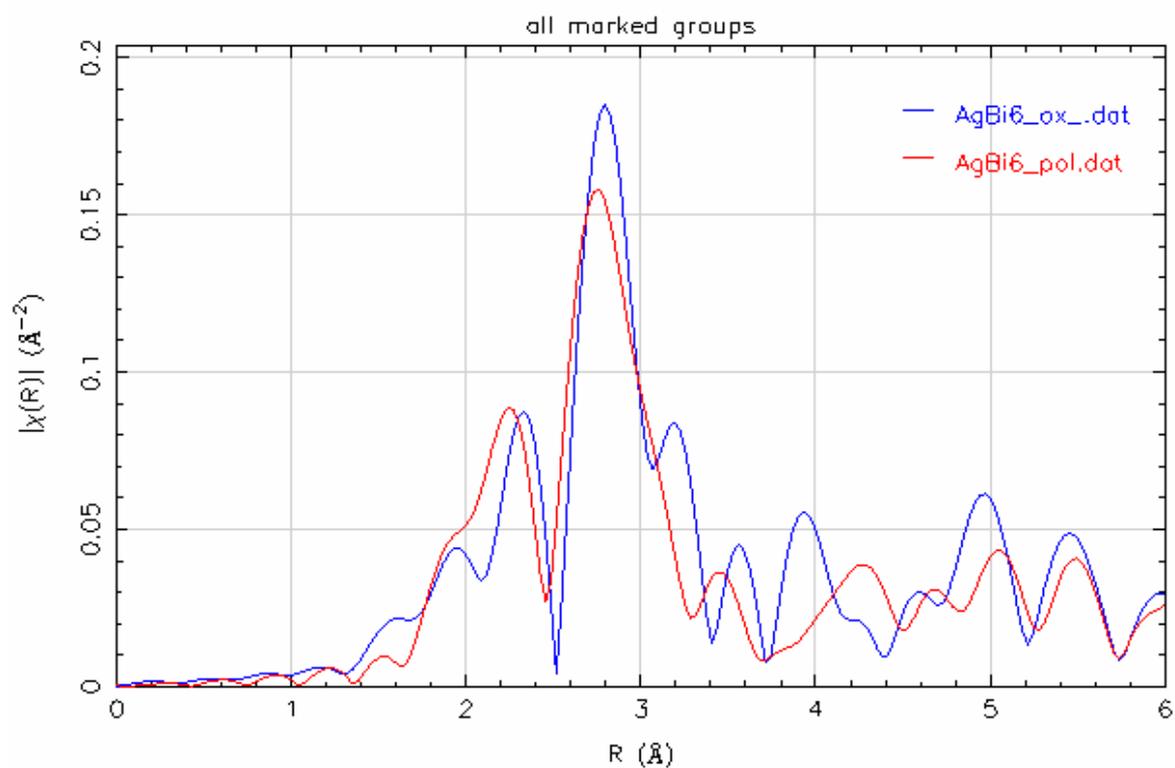


Figure 1. Radial Distribution Function (Bi edge) of the AgBi6 polished (red) and AgBi6 oxidised (blue) samples.

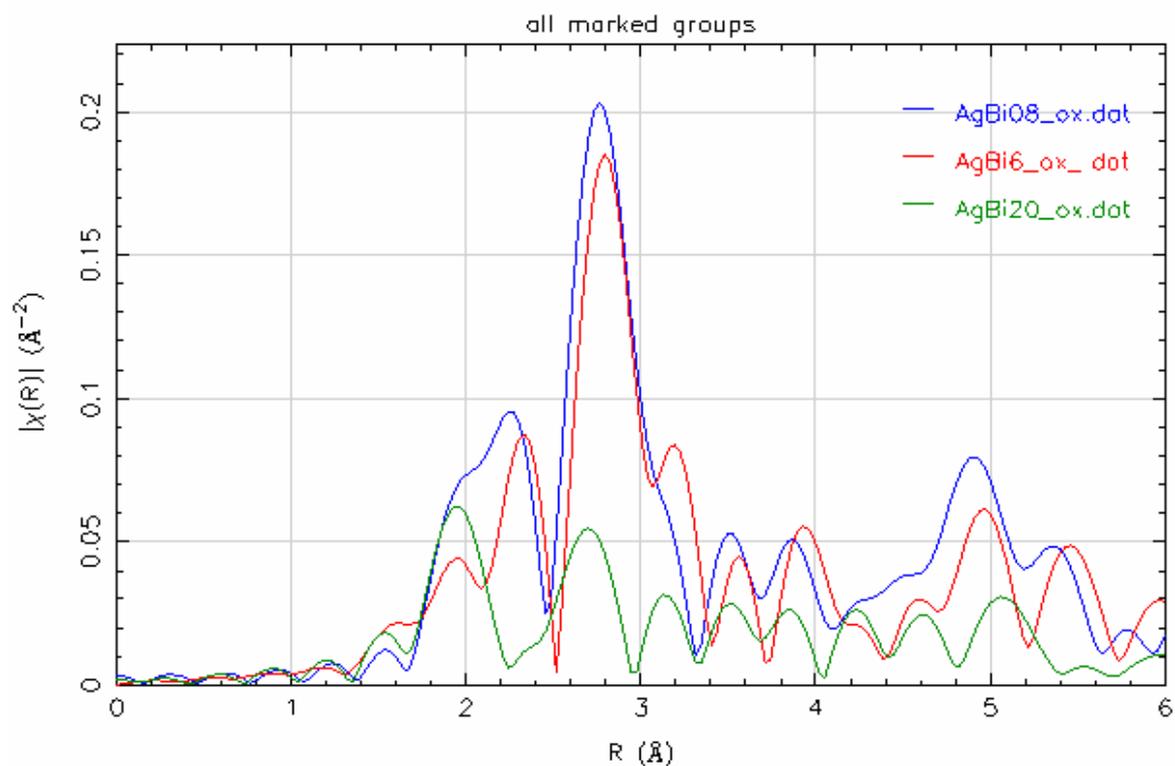


Figure 2. Radial Distribution Function (Bi edge) of oxidised samples of AgBi08 (blue), AgBi6 (red) and AgBi20 (green).

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