In Situ X-ray Diffraction Investigations of Hydrogen Absorption in Nanocrystalline Ti₂RuFe Alloy During Cathodic Hydrogen Discharge

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Introduction

Nanocrystalline Ti-Ru-Fe alloys prepared by high-energy ball milling were shown to be effective electrocatalysts for hydrogen evolution in typical chlorate electrolysis conditions. For example, at 250 mA cm^{-2}, the cathodic overpotential is reduced by 250 mV compared to that of conventional steel cathodes.[1] However, the stability of these oxygen-free compounds is limited, and decrepitation occurs upon prolonged operation.[2] Based on a series of electrochemical measurements performed in a NaOH electrolyte, it was suggested that degradation occurs via the penetration of hydrogen in the electrode material during the cathodic reaction.[3,4] In order to find some direct evidence for this mechanism, *in situ* x-ray diffraction measurements were performed on nanocrystalline Ti-Ru-Fe alloy as a function of the electrode potential.

Methods and Materials

For this study, a specially designed electrochemical cell (EC) with a moveable piston on which the working electrode was mounted was used. The EC was operated in two different modes. On one hand, when the sample is in its lowest position, the thickness of the electrolyte layer between the surface of the working electrode and the Kapton window is about 1.5 cm. In that position, there is no limitation due to the diffusion of the reacting species to the electrode. However, the thickness of the electrolyte layer prevents measurements with low-energy x-rays to be done. On the other hand, the working electrode could also be brought in its highest position, where the electrolyte thickness is reduced to a few hundreds of microns. In that configuration, the hydrogen discharge reaction cannot proceed to any significant extent due to severe diffusion limitations. However, the reduced electrolyte thickness does allow x-ray diffraction measurements (at 7.66 keV) to be realized. The working electrode can be moved from its lower to its higher position while the electrode potential is kept constant.

In this cell, the counter electrode is a Pt wire placed around the working electrode. A saturated calomel electrode is used as a reference electrode and the electrolyte was H₂SO₄ 1N. The whole cell could be fitted in a cell holder designed to fit in the goniometer of beamline 8-ID (Fig. 1). The experiment was performed in the following way. First the initial x-ray diffraction pattern (before) was recorded at open circuit potential with the electrode in the upper position. Then the electrode was brought in its lower position and a cathodic potential (-0.7 V) was applied for 60 minutes. Strong hydrogen evolution was observed during this period. Two peristaltic pumps were used to remove the hydrogen gas from the EC and to maintain a constant level of electrolyte in the cell. Then the working electrode was brought in its upper position
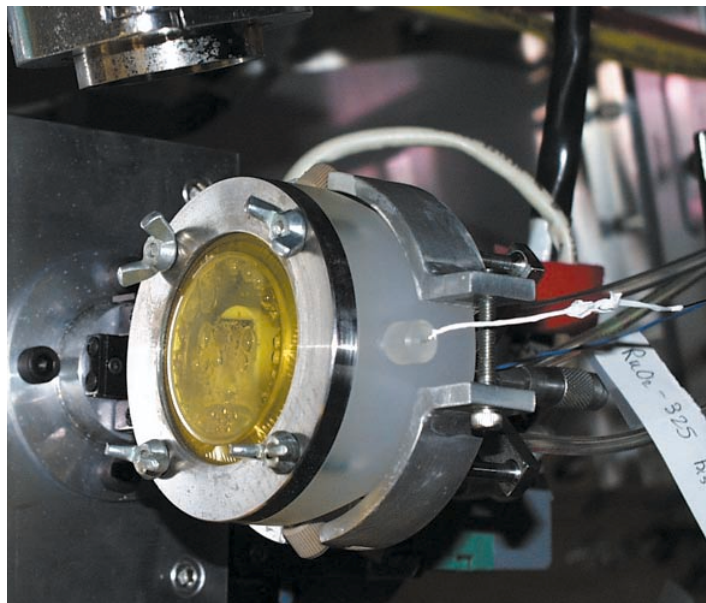

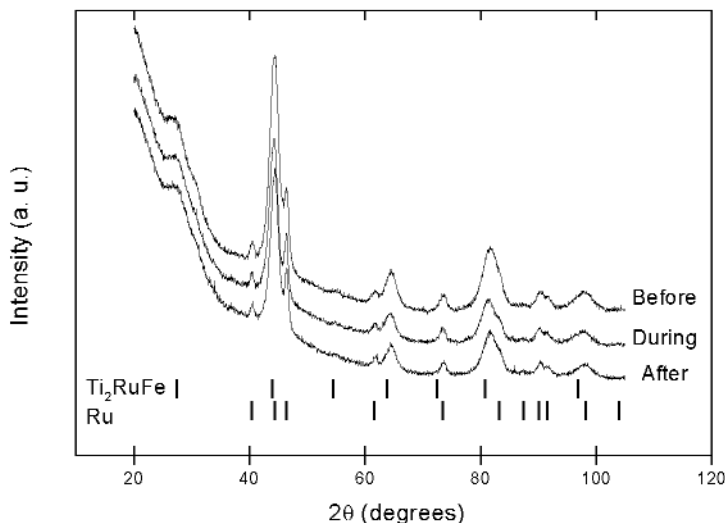FIG. 1. Image of the electrochemical cell installed on beamline 8-ID.

FIG. 2. X-ray diffraction patterns of nanocrystalline Ti₂RuFe.

while maintaining the electrode potential at the same value. The x-ray diffraction pattern (during) of the sample was taken while the electrode was at that potential. Finally, the electrode was moved back to the lower position, and the electrode potential was allowed to reach its open circuit value. The x-ray diffraction pattern (after) was again recorded in that state.

This experiment was carried out on the time-resolved x-ray scattering setup installed on the 8ID-D side station.[5] The 7.66-keV x-ray beam had a dimension of 0.6×0.9 mm^2 and a flux just above 10^{12} photons per second for a storage ring current of 100 mA. The detector was a scintillator counter. Rietveld analysis was performed using GSAS, a software that allows the fitting of x-ray diffraction spectra.
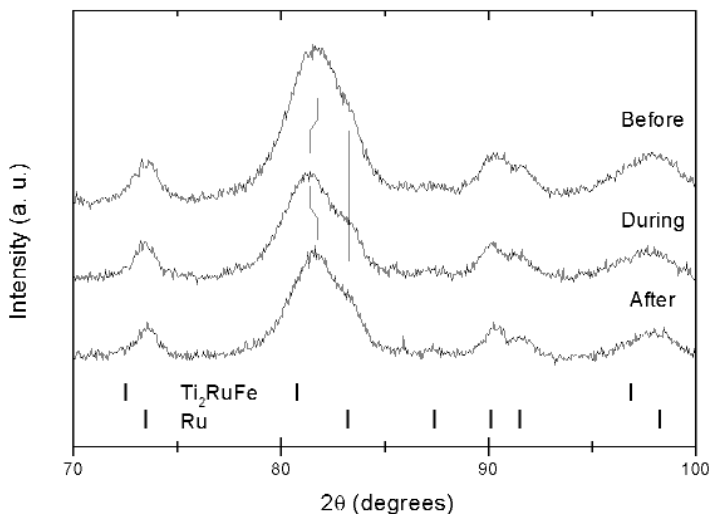

FIG. 3. X-ray diffraction patterns of nanocrystalline Ti$_2$RuFe.

Results and Discussion

In situ x-ray difffraction patterns of nanocrystalline Ti-Ru-Fe (2-1-1) alloy before, during, and after electrolysis are shown in Figs. 2 and 3. Nanocrystalline Ti-Ru-Fe alloy with a 2-1-1 composition is made of two distinct phases: a simple cubic (CsCl) B2 phase, whose stoichiometry is Ti$_2$RuFe (97 wt.%) and hexagonal Ru (3 wt. %). Upon cathodic polarization (during) there is a small but noticeable shift of the diffraction peaks of the B2 phase towards smaller 2θ angle values. This shift is more easily discernible at wide angles. For example, Fig. 3 shows an expanded view of Fig. 2 in the vicinity of $2\theta = 80°$. The shift of the (211) peak of Ti$_2$RuFe towards smaller 2θ values is clearly noticeable. This shift correponds to an increase in the lattice parameters following the incorporation of hydrogen in the cubic lattice. It is interesting to note that this shift of the (211) peak is totally reversible, as it returns back to its original position when the electrode is open-circuited.

Table 1 : Results of the Rietveld analysis

	Lattice parameter (Å)			Crystal size (nm)		Phase concentration (wt. %)	
	Ru		B2	Ru	B2	Ru	B2
	a	c	a				
before	2.700	4.272	3.034	17	7	8.3	91.7
during	2.702	4.277	3.043	16	6	7.1	92.9
after	2.699	4.273	3.033	13	7	10.3	89.7

The results of Rietveld refinement analysis (Table 1) show that the lattice parameter expands during hydrogen evolution. The expansion of the unit cell is about 0.3%. As suggested previously, this reaction is totally reversible and the lattice parameter returns to its original value when the electrode is open-circuited. For comparison, change in the lattice parameter of hexagonal Ru, which does not absorb hydrogen, is less than 0.03%. As far as we can tell by the Rietveld analysis, there is no change in the crystallite size and the concentration of both phases.

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