Surface segregation and oxidation of Pt$_3$Ni(1 1 1) alloys under oxygen environment

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ABSTRACT

Utilizing ambient pressure X-ray photoelectron spectroscopy (AP-XPS), the surface segregation and oxidation of Pt$_3$Ni(1 1 1) alloys are investigated as a function of temperature and oxygen pressure. The *in situ* AP-XPS measurements of oxygen oxidation process show that the Pt "skin" surface is not stable under the exposure of oxygen pressure of 100 mTorr at room temperature. As the temperature and pressure are elevated, the formations of Ni$_2$O$_3$, NiO$_x$, and NiO are observed on surface while Pt atom starts to reduce its adsorbed oxygen, which is a clear sign of surface segregation of Ni to surface. Upon the evacuation of oxygen gas, *i.e.* ultrahigh vacuum condition, both of NiO$_x$ and NiO oxide get reduced and Ni$_2$O$_3$ remains on the surface. The DFT calculation is employed to explain the formation of surface oxides under oxidation condition.

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Among many candidates for next generation fuel cells, the polymer membrane fuel cell (PMFC) shows many advantages over other competing ones, including low temperature operation and environmental friendliness. However, a slow oxygen reduction rate (ORR) at cathode in PMFC remains as the main obstacle, and the high cost of Pt as a cathode material limits the practical applications of hydrogen fuel cell technology. Although no substitutes for Pt have yet been found for catalytic materials for cathode materials in fuel cell, the recent reports [1,2] have shown that the rate of ORR in PMFC is improved by 80 times when the Pt is alloyed with certain 3d transition metals (TM) at around 25% of total concentration. The reports showed the presence of Pt "skin" layer (Pt-Skin) formed during electrochemical measurements, and further pointed out the altered surface electronic structures from the formation of the Pt skin layer as the origin of the enhanced chemical reactivity [3,4].

Immediately after the reports came out, tremendous amounts of efforts have been devoted to fabricate or synthesize the material that can reproduce or mimic the chemical reactivity found in model system. In the meantime, it has been shown that reactivity of surface can be controlled by adjusting the degrees of TM metal surface segregation, based on the thermodynamics and kinetics of bimetallic systems under oxygen exposure. Out of immense investigations, many groups in this field learn that the structure of Pt skin layer is not stable under reaction conditions and the subsurface 3d TM can be easily segregate to the surface layer under the operating conditions [5,6]. The TM has higher electronegativity than Pt and it segregates to the surface under the elevated oxygen pressure and even at low temperature, leading to the degradation of surface reactivity. As well known, the stability in electrochemistry is one of the critical factors to consider for its successful application to fuel cell. Consequently, the issues of surface segregation of TM in Pt$_3$TM system and its loss of reactivity have become the most important problems to resolve [7,8].

Previously, the stability of Pt-3d TM system was investigated with DFT calculation, showing the structural evolution under various reaction conditions [7]. According to the report, Pt-skin surface is more stable under reductive condition, *i.e.* ultrahigh vacuum condition (UHV) and CO conditions, while 3d TM-skin surface become more stable under oxidizing condition. Furthermore, the group looked into the case of oxygen induced segregation of Pt$_3$Ni(1 1 1) system and calculated the corresponding phase diagram [8]. According to their calculation, under UHV condition, the Pt-skin surface is energetically more stable. However, with increase of oxygen chemical potential, the stronger O—Ni bonding strength can overcome the cost of segregation energy and the surface forms Ni-enriched surface layer with oxygen coverage higher than 0.50 ML. One thing to note here is that Pt skin surface is not stable in the argument of surface energy, *i.e.* Pt has higher surface energy compared to the one of the Ni. In the case of this particular system, strain effect can explain the situation better. Pt atoms in Pt$_3$Ni bulk are under the compressive strain compared to the Pt bulk parent, whereas Ni atoms in Pt$_3$Ni are under the expansive strain compared to the Ni bulk parent. Accordingly, compared to their bulk parents, the surface energy for Pt-skin of Pt$_3$Ni would decrease because of stronger inner-layer interaction under the compressive strain, but for Ni skin of Pt$_3$Ni increase under the expansive strain. This might lead to the Pt-skin more favorable than that of the Ni-skin, as found in experiment, though opposite to the order of the Pt and Ni surface energies/cohesive energies for their bulk parents.

In the meantime, in 2013, with the use of XPS, X-ray absorption spectroscopy (XAS), and electron energy loss spectroscopy, A. Politano et al. reported the evidence of Ni segregation and the formation of NiO$_x$ surface oxide upon the exposure of Pt$_3$Ni(1 1 1) surface to the oxygen gas at surface temperature of 600 K [9]. The group measured the Ni 3p core-level XPS spectra and Ni L-edge XAS spectra to demonstrate the evidence of surface segregation and oxidation of Ni elements in Pt$_3$Ni(1 1 1). The conclusion of the report is that the oxygen atom bonds on Ni atom, showing no sign of Pt associated to oxygen as expected. However, it is to note that the entire measurements of the report are carried out by means of *ex situ* measurement, *i.e.* the process of oxidization was carried out separately prior to the measurements and entire measurements are carried out under UHV condition. In addition, the group used the analysis of Ni 3p core-level peak for extracting the oxidation state information. However, in this particular system, Ni 3p level is not suitable choice for identifying exact oxidation state since the Ni 3p peak heavily influenced by the background of Pt 4f peak in the Pt$_3$Ni alloys.

In early 2014, C. Chen et al. reported the successful fabrication of 3-dimenstional Pt$_3$Ni nanoframes exhibiting nano-segregated Pt-skin structures with both enhanced reactivity and durability [10]. The group fabricates the open-framework structures composed of 2 ML of Pt-covered surface with Ni atom inside by transforming the PtNi$_3$ polyhedra to Pt$_3$Ni nanoframes with preferential etching under solution. Interestingly, this group utilized the Ni segregation property under oxygen pressure to produce the Pt-skin layer out of nanoframes and made it stable under reaction condition. This report demonstrated that the surface segregation effects can be well utilized so that ideal surface composition can be achieved in nano-scale alloys system.

In this report, we present the real-time *in situ* measurement of surface segregation of Ni atoms on Pt$_3$Ni(1 1 1) surface under oxygen pressurized condition. With ambient pressure X-ray photoelectron spectroscopy (AP-XPS), the *in situ* measurements of oxygen oxidation process are carried out on Pt$_3$Ni(1 1 1) surface and the stability of Pt "skin" surface is examined as a function of temperature and pressure. In order to resolve the oxidation states of Ni during the segregation/oxidation processes, both of O 1s and Ni 2p core-level spectra are measured simultaneously
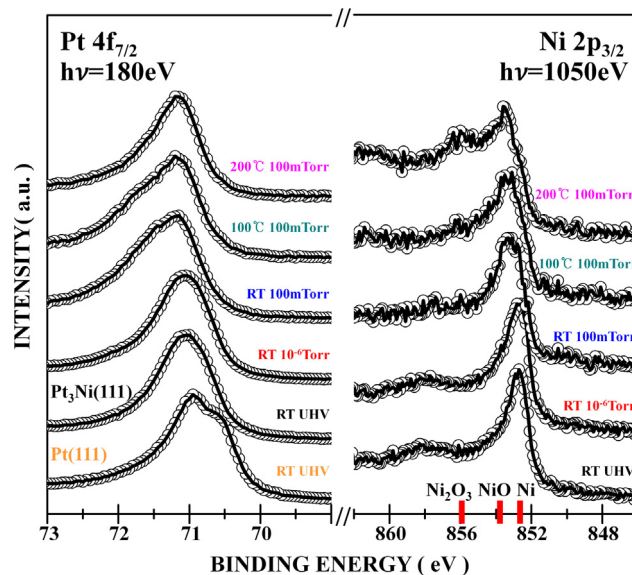

Fig. 1. Pt 4f and Ni 2p core-level spectra measured as a function of oxygen gas pressure and temperature.

under *in situ* oxidizing condition. At room temperature, there is no clear indication of Ni segregation to surface up to the oxygen pressure of 10^{-6} Torr. However, as the oxygen pressure is increased to 100 mTorr at room temperature, the Ni$_2$O$_3$ and NiO$_x$ oxide starts to appear at the surface. When the sample temperature is increased to 100 °C under 100 mTorr of oxygen pressure, the NiO oxide starts to form on the surface. All the portion of Ni-oxides compounds, Ni$_2$O$_3$, NiO$_x$, and NiO, continuously grow when the surface temperature is further increased to 200 °C. Upon the removal of oxygen gas to UHV, *i.e.* the reducing condition, both of NiO$_x$ and NiO oxide get reduced significantly, yet Ni$_2$O$_3$ oxide becomes significantly increased. To understand the thermodynamics of oxidation processes in Pt$_3$Ni(1 1 1), DFT calculation is employed.

The AP-XPS measurements are carried out at soft-ray beamline BL13 at Photon-Factory of High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan [11] and BL9.3.2 at Advanced Light Source of Lawrence Berkeley National Laboratory, USA [12]. The details of AP-XPS endstations on both synchrotron radiation facilities can be found elsewhere [13]. The Pt$_3$Ni(1 1 1) single crystal is provided by MaTek Inc. and the clean surface is prepared with repeated cycles of sputtering and annealing processes as previously described in the literature [4]. The surface cleaning cycle was repeated until no trace of carbon and oxygen species are detected by XPS. Before the experiment, the surface condition was checked by LEED and the well-ordered LEED patterns are observed, identical to previous report [4]. The gas pressure was controlled by UHV metal leak valve and the sample heating was made by using pyrolytic boron nitride (PBN) heater from the backside of sample.

For theoretical calculation, spin-polarized density functional theory calculations were performed using Vienna Ab-initio Simulation Package (VASP) [14,15], employing the all-electron projected augmented wave (PAW) potentials [16,17], and the Perdew-Wang 91 (PW91) exchange-correlation functional [18]. The wave function was expanded by plane wave with kinetic cutoff of 400 eV. A grid of (12 × 12 × 12) Monkhorst-Pack grid (containing the Γ point) was used for the Brillouin zone k points sampling for bulk calculation. The optimized lattice constants for the bulk Pt (fcc), NiO (rock salt), and Pt$_3$Ni (L1$_2$) are 3.99, 4.19, 3.89 Å, respectively. The total energy of O$_2$ was corrected by using the experimental enthalpy of water [19].