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Charge exchange between low energy alkali ions and cerium oxide surfaces

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Abstract

The fraction of low energy Na^+ ions neutralized during single scattering from $CeO_2(100)$ surfaces was measured with time-of-flight spectroscopy. The projectile ionization level is resonant with the surface electronic states, so that the neutralization results from a non-adiabatic charge exchange process that depends on the exit velocity and the local electrostatic potential (LEP) along the exit trajectory at a point close to the surface. Variations of the measured neutral fraction with ion energy and exit angle differ from the results obtained from clean metals due to the inhomogeneity of the LEP on an oxide surface. The results suggest that neutral fraction data collected as a function of emission angle and ion energy could be used to quantitatively map the shape of an inhomogeneous LEP.

Keywords: Low energy ion scattering (LEIS); Ion–solid interactions; Surface electronic phenomena; Cerium oxide; Metal oxide surfaces; Low index single crystal surfaces; Insulating surfaces

1. Introduction

CeO_2 has interesting catalytic properties, which presumably result from an electronic configuration that includes many valence electrons [1,2]. This material is also important as it has been used as a surrogate for studies of radioactive U and Pu oxides [3,4]. CeO_2 surfaces can be prepared in a fully oxidized or a partly reduced form [5]. The surface properties have been previously investigated with a limited number of experimental techniques, including X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) [5–10]. To completely understand the catalytic behavior and surface properties of these materials at a fundamental level, however, it is necessary to identify the localized electronic structure at the surface.

Low energy (0.5–10 keV) ion scattering from solids is well-established analytical technique for determining the composition and atomic structure of surfaces [11]. In addition, the neutralization of scattered alkali ions is sensitive to the electronic states near the Fermi level [12–15]. The dominant electron exchange mechanism in low energy alkali ion scattering is non-adiabatic resonant charge transfer (RCT), which occurs between the surface conduction band and the projectile ionization level [12]. The neutral fraction (NF) is determined along the outgoing trajectory at an effective "freezing point", which is typically on the order of 1 Å above the surface. The measured NF depends on the relative position of the ionization level and the surface Fermi level at that point, and may be modified by the specific local electrostatic potential (LEP). In general, the ionization potential of the alkali ion is greater than the surface work function, so that in the adiabatic case all of the scattered particles would be neutralized. For a collision of low energy ions, however, the interaction time is small so that the charge exchange becomes non-adiabatic and the resulting charge distribution is determined while the projectile is close to the surface. For a metal with a homogeneous LEP, this process normally leads to an increase in the NF as the work function is lowered or the perpendicular component of the exit velocity is decreased.

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The electrostatic structure of a metal oxide surface is more complex than that of a pure metal, as there are elements in distinct charge states that give rise to an inhomogeneous LEP. Neutralization in large-angle alkali ion scattering is sensitive to the inhomogeneous LEP associated with electropositive and electronegative adsorbates on metal surfaces [13,18–29], and should therefore also be useful in probing an inhomogeneous metal oxide surface [30]. Previous experiments investigating charge exchange between low energy projectiles and metal oxide surfaces [16,17] were performed in a small scattering angle configuration ($\leqslant 7°$), which does not allow for separation of scattering from different sites.

In this paper, low energy alkali ions are scattered at large angles from $CeO_2(100)$ surfaces, and the NF of $^{23}Na^+$ ions singly scattered from the Ce sites is measured with time-of-flight (TOF) spectroscopy. It is found that the neutralization decreases for more grazing angles and increases for higher energy, in contrast to the usual expectations for scattering from a homogeneous surface. This behavior directly reflects the inhomogeneity in the surface potential, and demonstrates that NF data potentially could be used to experimentally image an inhomogeneous LEP.

2. Experimental procedure

The experiments were performed in an ultra-high vacuum chamber (base pressure = 5×10^{-11} Torr) that contains standard surface analysis tools, including X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) [15,22]. The $CeO_2(100)$ single crystal substrate ($10 \times 10 \times 1$ mm^3, Commercial Crystal Laboratories) was mounted to a Ta holder, and a calibrated infrared pyrometer was used to measure the sample temperature during annealing. The surface was cleaned by cycles of 500 eV Ar^+ ion bombardment and annealing at 873 K until a (1×1) LEED pattern was obtained. The purity and chemical state of the surface region were checked with XPS. The work function of the sample was measured by monitoring the position of the secondary electron cutoff with an electrostatic analyzer while 200 eV electrons were incident on the sample.

Note that metal oxides are generally insulators, so that charging of the surface can hinder charged particle measurements. Some metal oxides such as $TiO_2(110)$ [31] and CeO_2 [32] become semi-conducting after an annealing treatment, however, so that charged particle spectroscopy can be performed. There were no indications that charging affected these measurements.

Ion scattering spectra were collected for scattering along the [001] azimuth. TOF was used to measure the charge state-resolved kinetic energy distribution of the scattered particles [13]. The 1.0–4.5 keV $^{23}Na^+$ beam was deflected across a 1.0 mm^2 aperture to produce 40-ns pulses at a rate of 80 kHz. The ions and neutrals scattered at 150° were detected by a dual microchannelplate (MCP) array after traveling through a 0.55 m long flight tube containing a pair of stainless steel deflection plates. “Total Yield” spectra were collected with the deflection plates held at ground, while “Neutrals Only” spectra were collected by placing 300 V between the plates to deflect the scattered ions.

For most of the measurements, the surface was held at room temperature. Some ion scattering measurements were performed at lower temperatures, however, by cooling with liquid nitrogen, while others were performed with the sample at elevated temperature.

3. Results

Data was collected from both the fully oxidized and partially reduced surfaces, which can be reversibly prepared by annealing in oxygen or vacuum, respectively. Fig. 1 shows Ce 3d XPS spectra for the fully oxidized surface and for the partially reduced surface. After annealing at 873 K in 10^{-6} Torr of dry O_2, a stoichiometric oxide surface is obtained; after annealing in UHV, however, a partially reduced surface is formed due to oxygen vacancies caused by thermal desorption [5,33]. The $Ce3d_{5/2}4f^1$ component becomes visible with the conversion of some surface Ce^{4+} sites into Ce^{3+} [33]. The work function of the oxidized $CeO_2(100)$ surface was measured to be ~4.6 eV, while the work function of the reduced surface was about 0.3 eV lower. It should be noted, however, that the preparation is not entirely reproducible, so that work function variations on the order of a few tenths of an eV would occur for different samples prepared in the same manner. Such work function changes can have a pronounced effect on a measured NF, and as such they must be carefully monitored.

Fig. 2 shows representative TOF spectra collected by scattering 3.0 keV Na^+ from the partially reduced $CeO_2(100)$ surface. The upper spectrum shows all of the scattered particles, while the lower spectrum shows the neutrals that remain after the scattered ions are deflected away. The spectra are displayed with respect to flight time, such that longer times correspond to lower scattered kinetic energies. Each spectrum is dominated by a sharp single

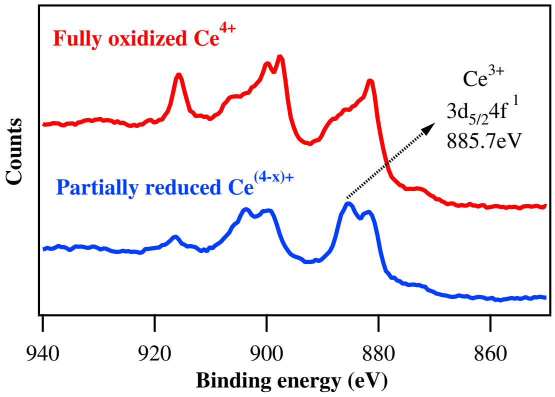

Fig. 1. XPS spectra of the fully oxidized and partially reduced $CeO_2(100)$ surfaces.