Late Breaking Session
Room: 109 - Session SS2-FrM

Surface Science Late Breaking Session
Moderator: C.R. Eddy Jr., U.S. Naval Research Laboratory, S.B. Sinnott, University of Florida

8:20am **SS2-FrM1 CO Oxidation Facilitated by Robust Surface States on Au-Covered Topological Insulators**, ***H. Chen***, The University of Tennessee, Knoxville, *W. Zhu*, The University of Tennessee, Knoxville and ORNL, *D. Xiao*, Oak Ridge National Laboratory, *Z. Zhang*, Univ. of Sci. and Tech. of China and The Univ. of Tennessee, Knoxville

Surface states—the electronic states emerging as a solid material terminates at a surface—are usually vulnerable to contaminations and defects. The robust topological surface state(s) (TSS) on the three-dimensional topological insulators (3DTI) provide a perfect platform for exploiting surface states in less stringent environments. Employing first-principles density functional theory calculations, we demonstrate that the TSS can play a vital role in facilitating surface reactions by serving as an effective electron bath. We use CO oxidation on gold-covered Bi_2Se_3 as a prototype example, and show that the robust TSS can significantly enhance the adsorption energy of both CO and O_2 molecules, by promoting different directions of electron transfer. The concept of TSS as an electron bath may lead to new design principles beyond the conventional *d*-band theory of heterogeneous catalysis.

*H. Chen, W. G. Zhu, D. Xiao, and Z. Y. Zhang, Phys. Rev. Lett. 107, 056804 (2011)

8:40am **SS2-FrM2 A Theoretical Study of Methanol Synthesis from CO_2 Hydrogenation on Metal-doped Cu(111) Surfaces**, ***Y. Yang***, State University of New York (SUNY) at Stony Brook, *M.G. White*, Stony Brook University and Brookhaven National Laboratory, *P. Liu*, Brookhaven National Laboratory

The synthesis of methanol (CH_3OH) from CO_2 hydrogenation ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) has attracted considerable attention in the past decades. It is not only industrially important, but also of great environmental significance due to its application in the conversion of greenhouse gas, CO_2. Commercially, the reaction is performed on a catalyst containing Cu, ZnO and Al_2O_3, on which the conversion of CO_2 to CH_3OH is kinetically limited to 15-25%. To improve the performance of the Cu catalysts, the effect of alloying on CH_3OH synthesis was investigated in this study.

Density functional theory (DFT) calculations and Kinetic Monte Carlo (KMC) simulations were employed to investigate the CH_3OH synthesis reaction from CO_2 hydrogenation on metal-doped Cu(111) surfaces. Both the formate pathway and the reverse water gas shift (RWGS) reaction followed by CO hydrogenation pathway (RWGS + CO-Hydro) were considered. Our calculations showed that the overall CH_3OH yield increased in the sequence: Au/Cu(111) < Cu(111) < Pd/Cu(111) < Rh/Cu(111) < Pt/Cu(111) < Ni/Cu(111). On Au/Cu(111) and Cu(111), the formate pathway dominates the CH_3OH production. Doping Au does not help the CH_3OH synthesis on Cu(111). Pd, Rh, Pt and Ni are able to promote the CH_3OH production on Cu(111), where the conversion via the RWGS + CO-Hydro pathway is much faster than that via the formate pathway. Further kinetic analysis revealed that the CH_3OH yield on Cu(111) was controlled by three factors: the dioxomethylene hydrogenation barrier, the CO binding energy and the CO hydrogenation barrier. Accordingly, two possible descriptors are identified which can be used to describe the catalytic activity of Cu-based catalysts towards CH_3OH synthesis. One is the activation barrier of dioxomethylene hydrogenation; the other is the CO binding energy. An ideal Cu-based catalyst for the CH_3OH synthesis via CO_2 hydrogenation should be able to hydrogenate dioxomethylene easily and bond CO moderately, being strong enough to favor the desired CO hydrogenation rather than CO desorption, but weak enough to prevent CO poisoning. In this way, the CH_3OH production via both the formate and the RWGS+CO-Hydro pathways can be facilitated.

9:00am **SS2-FrM3 Synthesis and Characterization of Surface Oxide Films on CoGa(100)**, ***D.C. O'Connor***, Stony Brook University, *S. Axnanda, W.-P. Zhou*, Brookhaven National Laboratory, *M.G. White*, Stony Brook University and Brookhaven National Laboratory

Methanol is currently garnering a lot of attention as both a chemical feedstock for synthesis of organic substances and as a possible source of energy. It is currently produced industrially from a mix of syngas and hydrogen over a copper-zinc oxide catalyst. However, it has been shown that palladium-gallium oxide is a more active catalyst for methanol production, and uses a carbon dioxide-hydrogen feed, which is desirable for efforts toward CO_2 mitigation[1, 2]. Surface Science characterization of this catalyst poses a problem as a gallium oxide substrate is not conductive enough for use with X-ray photoelectron spectroscopy (XPS) or low energy electron diffraction (LEED). The most straightforward way to circumvent this limitation is to grow Ga_2O_3 on a conductive substrate. It has been shown that a Ga_2O_3 film forms on the surface of CoGa alloy crystals when exposed to oxygen[3, 4]. In this work we report the results of the characterization of Ga_2O_3 films on the CoGa(100) surface using XPS, LEED, and ion scattering spectroscopy (ISS). The films were synthesized using either O_2 or NO_2 as the oxidant at 300 K or in excess of 700K. ISS scans showed that cobalt was always present in the top surface layer regardless of oxidation conditions. XPS illustrated that depending on the oxidant and the temperature, the composition of the oxide films vary with some being nearly all Ga_2O_3 and ordered and others Co-Ga mixed oxides that gave no diffraction pattern.

1. Fujitani, T., Saito, M., Kanai, Y., Watanabe, T., Nakamura, J., Uchijima, T., *Appl. Catal. A* **1995,** 125, L199.
2. Collins, S. E., Balatanás, M.A., Bonivardi, A.L., *J. Catal.* **2004,** 226, 410.
3. Pan, F. M., Pflitsch, C., David, R., Verheij, L., Franchy, R., *Surf. Sci.* **2001,** 490, L609.
4. Vlad, A., Stierle, A., Marsman, M., Kresse, G., Costina, I., Dosch, H., Schmid, M., Varga, P., *Phys. Rev. B* **2010,** 81, (11), 115402.

9:20am **SS2-FrM4 Apparent Ferroelectricity from Electrochemistry: Local Vacancy Diffusion in Oxides**, ***A. Kumar***, *Y. Kim, A. Tselev, S.V. Kalinin, A. Baddorf*, Oak Ridge National Laboratory

Multiple reports of unexpected ferroelectricity in nanoscale systems have been made based on electromechanical hysteresis detected by piezoresponse force microscopy (PFM). These include thin films of ferroelectric materials below theoretical stability limits and materials without bulk ferroelectricity, such as strontium titanate and manganites. However, recent studies of ionic systems, such as Li-ion conductors, suggest that local electrochemistry, usually ignored in these studies, may have an important role to play in the origin of the hysteresis loops. We report the role of local electrochemistry, including surface and bulk oxygen vacancy generation and dynamics on ionic conductors such as Yttria stabilized zirconia (YSZ) and lantanum strontium cobaltites (LaSrCoO) and compare results with less understood systems including strained and unstrained $SrTiO_3$ and the lantanum aluminate - strontium titanate (LAO-STO) interface.

The role of oxygen vacancies in oxides, of obvious relevance in fuel cells, memristors, superconductors, etc., have traditionally been studied in macroscopic volumes and has been limited by high activation temperatures. We have developed an approach for spatially resolved local assessment of the thermodynamics and kinetics involved in the generation and diffusion of oxygen vacancies by utilizing volume variations of these oxides upon application of a concentrated electric field. In band excitation electrochemical strain microscopy (ESM), a strongly confined electric field at a tip is used to drive the oxygen vacancies in these oxide materials and the tip used to detect the resulting local electrochemical strain due to migration of oxygen vacancies. Vacancy diffusion is relatively slow, so that local strain hysteresis loops are open. Mapping the loop opening as a function of the final bias establishes the onset and kinetics of the diffusion process. Signal relaxation experiments locally characterize the diffusion dynamics of the vacancies. In mixed ionic-electronic oxide systems, current-voltage measurements provide complementary information on electronic transport.

Mapping of local oxygen vacancy diffusivity with 30 nm resolution has been achieved on a number of oxides ranging from purely ionic conductors (YSZ) to mixed ionic electronic conductors (LaSrCoO), including ferroelectrics and resistive switching in TiO_2 and $SrTiO_3$ films. This approach was further applied to the LAO-STO interface, now a prototypical 2D electron gas with ferroelectric behavior proposed due to local hysteresis loops. While the role of *static* oxygen vacancies has been well discussed, we explore the local *dynamic* processes in the system. We observe two parallel dynamic processes that we tentatively ascribe to surface charge dynamics and bulk vacancy injection. This behavior is unique for LAO-STO and is not observed in YSZ and LaSrCoO. These observations both explain hysteresis without ferroelectricity and provide insight into the behavior of this system.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Office of Basic Energy Sciences, U.S. Department of Energy.

9:40am **SS2-FrM5 Dopant-enhanced Neutralization of Low Energy Li$^+$ Scattered from Si(111)**, *R.D. Gann*, University of California, Riverside, *Z. Sroubek*, Czech Academy of Sciences, Czech Republic, ***J.A. Yarmoff***, University of California, Riverside

The role of doping in semiconductor surface reactions is of fundamental scientific and technological importance, yet the effects of doping in atom-surface charge exchange have never been investigated directly. For example, in the dry processing of silicon, a dependence of oxidation, etching, and silicide formation rates on doping has been observed. The doping concentration changes the density of states at the surface by adding excess majority carriers, which could have a large effect on electron tunneling rates between reactants and the surface, leading to the observed doping dependences. In addition to populating the bands, the band gap of Si narrows with increasing dopant density, which may also influence charge exchange.

This work presented here demonstrates that the charge exchange between scattered low-energy Li ions and a passivated Si surface depends strongly on doping. The neutralization of 3 keV Li$^+$ ions scattered from Si(111) is measured as a function of doping density, dopant type, and hydrogen coverage using time-of-flight spectroscopy. When the surfaces are saturated with hydrogen to unpin the Fermi level, the neutral fractions decrease for lightly doped samples, but become anomalously large for highly doped *n*-type Si. The neutralization does not correlate with the surface work function, indicating that the models used for metal surfaces are not directly applicable here.

A model is presented that includes the many-body band-gap narrowing effect, which predicts the neutralization to good accuracy using a tunneling mechanism similar to the free-electron gas jellium model normally employed for ion/metal interactions, but excluding levels in the gap. This work demonstrates that the surface of Si behaves, as far as electron transfer is concerned, like a jellium electron gas with states missing in the band gap region.

10:00am **SS2-FrM6 Charge Transfer and Diabatic Dissipation of Surface Released Chemical Energy in GaP/Pt Schottky Nanostructures with a Resistively Heated Nanocathode Layer**, ***E.G. Karpov***, *S.K. Dasari*, *A. Hashemian*, University of Illinois

Recent observations of chemically induced hot electron flow over Schottky barriers in planar nanostructures provides interesting possibilities for electrolyte-free conversion of chemical energy into electricity and novel sensor applications. The work aims to make advantage of the nonthermal nature of the diabatic chemicurrents and explores the low-temperature (340-430K) chemovoltaic effect of hydrogen to water oxidation on Pt/GaP nanostructure surface. The chemicurrent is also studied at high pressures of the oxyhydrogen mixture diluted with nitrogen, all the way to atmospheric pressures. Separation of the diabatic component to the total generated current is performed with an accurate method based on resistive nanofilm heating.

10:20am **SS2-FrM7 Utilizations of Low Platinum Loading Pt-Co Bimetallic Alloy Catalyst for Proton Exchange Membrane Fuel Cells (PEM) in UHV Conditions**, ***A.S. Ahsen***, Gebze Institute of Technology, Turkey, *O.K. Ozdemir*, Yildiz Tech Univ., Turkey, *O. Ozturk*, Gebze Institute of Technology, Turkey

In this ongoing study it has been tailored surface structures and morphologies to increase chemical and structural stability for higher efficiency and improved utilization compared to presently available Pt-based catalysts used for fuel cell application. Pt-Co bi metallic alloys is selected to explore the electronic and structural properties of tailored surface and interfaces of electrocatalysts, and it is intended to explain surface chemical dynamics and interaction in fuel cell where chemical reaction pathways are influenced by the nature of the underlying support, the surfaces can be designed and modified appropriately to either promote or inhibit particular reaction.

A series of Pt and Pt-Co bi-metalic nanocatalysts alloys films were deposited on glassy-carbon disks and on a commercial hydrophobic carbon paper substrate by dc magnetron sputtering. The electronic structure and chemcial states o f surface were investigated by Photoelectron Spectroscopy (XPS and UPS). Cyclic Voltammetry (CV) and Rotating Disc Electrode (RDE) methods were used to investigate Active Surface Area (ASA) and Oxygen Reduction Reaction (ORR) kinetics . Low loading values, 6 -22 µg Pt/cm^2, were observed the kinetic properties of the nanocatalysts. The highest active surface area was observed with an optimum loading of 10 µg Pt/cm^2 value. Besides that the Pt-Co alloy catalysts showed significant improvement on catalytic activity against pure platinum catalysts. The effects of deposition temperature on alloy formation and reaction kinetics were also observed. A photoelectron spectroscopy study was also used for understanding electronic interaction between Pt and Co by the function of preparation temperature.

CV measurements indicate that carbon supported Pt-Co catalyst on gas diffusion electrode had electrochemical stability in the acidic environment. Also, it was observed that with increasing Co ratio metal oxidation and reduction current peaks rises. The enhancement on the ORR activity for the PtCo/C catalysts to form of the Pt-shell layer as revealed from the CV analysis, where the PtCo/C electrodes show a delayed formation of Pt-OH and faster reduction of the Pt-oxygenated containing species compared to Pt/C. It means that the oxophilicity of the PtCo/C catalysts are low compared to Pt/C. The hydrogen desorption peaks on the CV curve showed that the highest ESA value was obtained from Pt-Co(3:1) ratio. The capacitance region of PtCo catalysts increases with rising Co ratio. This is a strong evidence for that additional Co layers change the catalyst morphology. As a result, gas can reach to the reaction area easily and this reduces the ohmic resistance.

Authors Index

Bold page numbers indicate the presenter

— A —

Ahsen, A.S.: SS2-FrM7, **2**
Axnanda, S.: SS2-FrM3, 1

— B —

Baddorf, A.: SS2-FrM4, 1

— C —

Chen, H.: SS2-FrM1, **1**

— D —

Dasari, S.K.: SS2-FrM6, 2

— G —

Gann, R.D.: SS2-FrM5, 2

— H —

Hashemian, A.: SS2-FrM6, 2

— K —

Kalinin, S.V.: SS2-FrM4, 1
Karpov, E.G.: SS2-FrM6, **2**
Kim, Y.: SS2-FrM4, 1
Kumar, A.: SS2-FrM4, **1**

— L —

Liu, P.: SS2-FrM2, 1

— O —

O'Connor, D.C.: SS2-FrM3, **1**
Ozdemir, O.K.: SS2-FrM7, 2
Ozturk, O.: SS2-FrM7, 2

— S —

Sroubek, Z.: SS2-FrM5, 2

— T —

Tselev, A.: SS2-FrM4, 1

— W —

White, M.G.: SS2-FrM2, 1; SS2-FrM3, 1

— X —

Xiao, D.: SS2-FrM1, 1

— Y —

Yang, Y.: SS2-FrM2, **1**
Yarmoff, J.A.: SS2-FrM5, **2**

— Z —

Zhang, Z.: SS2-FrM1, 1
Zhou, W.-P.: SS2-FrM3, 1
Zhu, W.: SS2-FrM1, 1