

Thursday Afternoon, November 1, 2012

Energy Frontiers Focus Topic
Room: 15 - Session EN+AS-ThA

Characterization of Energy Materials and Systems

Moderator: L. Lohstreter, Medtronic, Inc.

2:00pm **EN+AS-ThA1 Growth Temperature and Stoichiometry Effects on the Inherent Stability of CdS/CdTe Solar Cells**, *D.S. Albin, T.A. Gessert, R. Dhere, S.-H. Wei, J. Ma, D. Kuciauskas, A. Kanevce, R. Noufi*, National Renewable Energy Laboratory **INVITED**

Capacitance-voltage (CV) measurements are commonly used to characterize semiconductor junctions. A common observation when performing such measurements on polycrystalline CdTe solar cells is that the measured capacitance is a strong function of the voltage scan direction. These results in a noticeable hysteresis in the C-V profile when capacitance data is collected using both forward (fwd) and reverse (rev) voltage scan directions. Similarly, hysteresis curves for the usual derived quantities such as net carrier density, N_a , and depletion width, W , naturally follows. We have recently observed that in particular, the hysteresis in calculated carrier acceptor density, $N_{a, \text{hys}}$, arbitrarily defined as $N_{a, \text{fwd}} - N_{a, \text{rev}}$ decreases as the CdTe growth temperature is reduced. At higher CdTe growth temperatures, this value is positive and shifts to negative values at lower growth temperatures. This behavior is believed to reflect a transition of the CdTe stoichiometry in CdS/CdTe solar cells from Cd-poor at higher temperatures to Cd-rich at lower temperatures based upon recently published CdTe binary phase diagrams.

The impact of Cd/Te stoichiometry on cell performance is suspected. Cd-poor stoichiometry favors the formation of Cd-vacancies (V_{Cd}), a beneficial acceptor, but it also simultaneously increases the formation of the Te antisite (Te_{Cd}), an important recombination center in CdTe. Recent theoretical calculations using the hybrid Heyd-Scuseria-Ernzerhof (HSE) functional also suggests that Te interstitials (Te_i) may be an important recombination center under Cd-poor conditions. Increased Cd chemical potential will reduce the formation of these recombination centers, but also reduce hole carrier density. Thus, an optimal growth condition, which could include extrinsic p-type doping, may be needed for leading to higher performance CdTe solar cells.

Not discussed to date however is whether stoichiometry has an inherent impact on the stability of CdTe solar cells. In this talk, we contrast accelerated lifetime study results for CdTe cells grown at different growth temperatures. Open-circuit voltage (V_{oc}) stability in cells grown at lower temperatures was noticeably improved. $N_{a, \text{hys}}$ in the latter cells was considerably smaller. Both V_{oc} and FF were well correlated with this capacitance-derived parameter. $N_{a, \text{hys}}$ was observed to be relatively unchanged in devices where V_{oc} did not degrade. Finally, time-resolved photoluminescence lifetimes of nearly 10 ns were measured in these cells made at lower temperatures relative to values of around 2 ns measured in higher temperature devices.

3:00pm **EN+AS-ThA4 XPS Characterization of Organic Gradients in Organic Photovoltaic and Organic Light Emitting Devices Using Ar GCIB Depth Profiling**, *S.N. Raman, J.S. Hammond, J.F. Moulder*, Physical Electronics

The use of organic materials for electronic applications such as Organic Photovoltaics (OPV's) and Organic Light Emitting Diodes (OLED's) is rapidly growing. The efficiencies of these devices are widely recognized to depend on the molecular gradients fabricated into the devices. Conversely, the degradation of these devices is suspected to depend on several factors including chemical degradation and chemical migration as a function of use. It is therefore very desirable to develop analytical techniques which can quantify chemical gradients as well as identify degradation products in these films.

Gas Cluster Ion Beam (GCIB) sources with low energy per atom $\text{Ar}_{2,000}^+$ ions have recently been demonstrated to provide a depth profiling technique for molecular species (1,2). GCIB depth profiling in an interleaved mode with the surface analysis spectroscopy of X-ray Photoelectron Spectroscopy (XPS) has been applied to model OPV and OLED devices. The 2 to 5 nm information depth of XPS, combined with the demonstrated "non-destructive" chemical information revealed after each GCIB sputter interval, facilitates the chemical gradient analysis of a series of model samples up to several 100 nm in depth with molecular depth resolution < 10 nm.

Selected model OPV and OLED samples were exposed to annealing and environmental degradation testing. The XPS depth profiles measured the

migration of organic components and dopants as a function of fabrication processes. This presentation will provide an overview of GCIB depth profiling with XPS as well as discuss the insights into efficiencies and degradation processes elucidated by this chemical gradient analysis technique.

1. T. Miyayama, et al. *Surf. Interface. Anal.* 42 (2010) 1453-1457.

2. T. Miyayama, et al. *J. Vac. Sci. Technology A*, 28 (2) (2010) L1-L4.

3:40pm **EN+AS-ThA6 Characterization of Degradation Mechanisms of Membrane Electrode Assemblies by XPS and SEM Imaging**, *A. Patel, K. Artyushkova, P. Atanassov*, University of New Mexico, *S. Wessel, V. Colbow, M. Dutta*, Ballard Power Systems, Canada

Durability of catalyst layer (CL) is of key importance in the deployment of PEMFCs. Catalyst layer (CL) degradation is linked to several failure mechanisms including Pt dissolution and agglomeration and support corrosion. X-ray photoelectron spectroscopy (XPS), a powerful technique to study chemical changes, has been applied to quantitatively analyze catalyst layer degradation in PEM fuel cells. More specifically, ionomer degradation was characterized by a decrease of CF_3 and CF_2 species and an increase in oxidized forms of carbon (e.g. C-O and C=O). Chemical speciation as determined by XPS for catalyst powders was correlated with electrochemical performance losses. MEAs using catalyst coated membranes that are composed of Pt catalyst supported on differing carbon supports were subjected to aging protocols to accelerate the degradation mechanisms of the cathode CL. In-situ and ex-situ diagnostics were used to quantify performance losses and structural changes of the CL.

Large area XPS was used for analysis of fresh, conditioned and aged cathode catalyst layers. Spectroscopic analysis, which provides an integral spectrum from approximately 1mm² area, may have a contribution from the GDL sublayer that was not fully removed from the catalyst layer side during separation of the MEA components. The GDL sublayer exhibits a peak in the same BE range as fully fluorinated carbons that are detected in the catalyst layer. Changes that have been detected in CL may not be due to the changes within the ionomer, but rather due to physical intermixing of layers caused by the testing protocols. XPS imaging enabled separation of the differing component contributions. Using Pt 4f imaging, regions are clearly identified where no Pt is present, indicating that GDL pieces adhere to the CL. Fluorine images at two different binding energies (one for the ionomer, and another for the GDL) confirm this. High resolution C 1s spectrum extracted from the area where catalyst is present does not show a high BE component in the C 1s spectrum of the area where GDL is present, confirming that the high BE component detected by large area spectroscopy are contributions from the GDL. High-resolution spectra acquired from the area where only catalysts layer is present shows higher amounts of oxidized forms of carbons. In addition, morphological changes of aged cathode catalyst layers have been evaluated by Digital Image Processing of SEM images for roughness, porosity and texture parameters.

4:00pm **EN+AS-ThA7 Selective Adsorption Behavior of CO₂ and C₂ Hydrocarbon Isomers over N₂ and Methane in a Flexible Metal Organic Frameworks**, *N. Nijem, P. Thissen*, University of Texas at Dallas, *P. Canepa*, Wake Forest University, *H. Wu, J. Li*, Rutgers University, *T. Thonhauser*, Wake Forest University, *Y.J. Chabal*, University of Texas at Dallas

Post combustion carbon capture is a complementary approach to research in renewable energy to combat the exponential increase of CO₂ emission and global warming. An important outcome of enhancing gas separation in materials, for example, is the decrease in energy needed for separation of hydrocarbons. Metal-organic Frameworks (MOFs) have shown promise in this area because their high surface area, porosity and chemical/structural tailorability contribute to the preferential selective adsorption of gases. This work explores the incorporation of CO₂ and hydrocarbons into a flexible framework, $\text{Zn}_2(\text{bpd})_2(\text{bpee})$, ($\text{bpd} = 4,4'$ -biphenyl dicarboxylate, $\text{bpee} = 1,2$ -bis(4-pyridyl)ethylene) using infrared (IR), Raman spectroscopy and van der Waals density Functional (vdW-DF) calculations. We present evidence for "gate opening" phenomenon, where the structure of the framework changes only upon adsorption of CO₂ and C₂ hydrocarbon isomers but not for N₂ or methane. Understanding the specifics of CO₂ interaction with the framework was explored to identify parameters affecting its selectivity. We find that the high quadrupole moment of CO₂ and its interaction through its carbon with the bpd linker induces the transformations. The flexibility of the framework was found to be primarily due to the specific connectivity of the Zn metal center to the ligands, at one end in a monodentate mode and at the other in a bidentate mode. The unexpected gate opening behavior in this same framework upon the adsorption of C₂ hydrocarbon isomers was also studied. We find that the

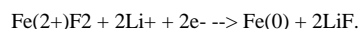
specific hydrogen bonding between the CH of the hydrocarbon and the C=O bond of the bpdc linker is responsible for this interesting behavior. Furthermore, the strength of the hydrogen bond was found to affect the gate opening pressure point. This effect points towards the potential of this framework for uses such as pressure swing adsorption based separation. In conclusion, we have identified specific interactions of CO₂ and hydrocarbons in a flexible framework that lead to their selective adsorption properties. This knowledge allows the design of frameworks with optimized properties.

4:20pm EN+AS-ThA8 Fabrication and Characterization of a PCBM-Terminated Organic Monolayer on a Si(111) Surface, T.J. Miller, A.V. Teplyakov, University of Delaware

The energy sector is a large, growing field in research and technology. A growing subset of the solar field is organic photovoltaics (OPV). Two areas that have long challenged researchers are efficiency and stability of the OPV devices. An area that is in need of fundamental understanding that may increase efficiency of these devices is the charge transfer. However, a precise nature of the bulk-heterojunction OPV donor/acceptor interface is difficult to pinpoint. Thus, model systems can be used initially to mimic these interactions. In the system presented here, the donor/acceptor interface is well-defined. Phenyl-C61-butyric acid methyl ester (PCBM) was reacted with an amino-terminated organic monolayer on a single crystalline Si(111) surface. Poly 3-hexylthiophene (P3HT) was then deposited onto this complex substrate, and the produced interface can be observed and investigated. Fourier transform infrared spectroscopy was used to identify the functional groups on the surface. The chemical and electronic states of the coating and the substrate were investigated by X-ray photoelectron spectroscopy, and the morphology was determined through atomic force microscopy. Preliminary charge carrier lifetime measurements will also be reported.

4:40pm EN+AS-ThA9 Conversion Reaction of Thin Film Metal Fluorides and Metal Oxides Exposed to Atomic Lithium, R. Thorpe, S. Rangan, R.A. Bartynski, Rutgers University

Modern Li-ion intercalation batteries use electrode materials that accommodate Li intercalation, enabling the exchange of Li ions during battery cycling without extensive alteration of the electrode's crystalline structure. Despite the stability of these materials to the intercalation process, the ability of such batteries to store energy is limited by the number of host sites in the electrodes to approximately one electron per formula unit. Conversion reaction materials could potentially store several times more energy than current generation batteries by utilizing the full range of charge states available to their constituent metal ions. For example, the following reaction occurs in a FeF₂ cathode:



Although conversion reaction materials have shown the promise of high energy storage density in electrochemical cells, their cycling stability is poor, and relatively little is known about the phase evolution and structural changes that occur during charge and discharge.

In order to study the fundamental properties of these materials, we have grown high purity thin films of conversion materials FeF₂, FeF₃, FeOF, FeO_x, and CoO. By exposing these films to atomic Li in vacuum, can follow the evolution of these materials as they approach the reaction products reached in the discharge of a conversion battery. We have used UV and inverse photoemission to measure the electronic structure of the valence and conduction bands respectively. Using these techniques in tandem, we are able to measure the band gap of these materials, which can then be related to their electronic conductivity. Using x-ray photoemission, we have measured the stoichiometry and valence states of the compounds involved in these reactions. In addition, we have examined the structure of these nano-scale materials using TEM and LEED.

For FeF₂, our XPS results show immediate reaction upon exposure to Li, fully reducing the Fe to the metallic state and forming LiF, with no evidence of intermediary phases in the film due to the high mobility of lithium. TEM of the initial and final films indicates a drastic morphology alteration, leading to a local precipitation of Fe₀ and LiF formation, with an overall particle size reduction from 10nm to 2nm, consistent with what is found in electrochemical studies.

However, the Li-CoO and Li-FeO_x reactions appear to diverge from the results of Li⁺ electrochemical reactions, leading to the simultaneous formation of both Li₂O and Li₂O₂, the latter of which hinders further reduction of the Fe and Co. These observations will be contrasted with results obtained from the related conversion reaction compounds FeO_xF_y and FeF₃.

Authors Index

Bold page numbers indicate the presenter

— **A** —

Albin, D.S.: EN+AS-ThA1, **1**
Artyushkova, K.: EN+AS-ThA6, **1**
Atanassov, P.: EN+AS-ThA6, **1**

— **B** —

Bartynski, R.A.: EN+AS-ThA9, **2**

— **C** —

Canepa, P.: EN+AS-ThA7, **1**
Chabal, Y.J.: EN+AS-ThA7, **1**
Colbow, V.: EN+AS-ThA6, **1**

— **D** —

Dhere, R.: EN+AS-ThA1, **1**
Dutta, M.: EN+AS-ThA6, **1**

— **G** —

Gessert, T.A.: EN+AS-ThA1, **1**

— **H** —

Hammond, J.S.: EN+AS-ThA4, **1**

— **K** —

Kanevce, A.: EN+AS-ThA1, **1**
Kuciauskas, D.: EN+AS-ThA1, **1**

— **L** —

Li, J.: EN+AS-ThA7, **1**

— **M** —

Ma, J.: EN+AS-ThA1, **1**
Miller, T.J.: EN+AS-ThA8, **2**
Moulder, J.F.: EN+AS-ThA4, **1**

— **N** —

Nijem, N.: EN+AS-ThA7, **1**
Noufi, R.: EN+AS-ThA1, **1**

— **P** —

Patel, A.: EN+AS-ThA6, **1**

— **R** —

Raman, S.N.: EN+AS-ThA4, **1**
Rangan, S.: EN+AS-ThA9, **2**

— **T** —

Teplyakov, A.V.: EN+AS-ThA8, **2**
Thissen, P.: EN+AS-ThA7, **1**
Thonhauser, T.: EN+AS-ThA7, **1**
Thorpe, R.: EN+AS-ThA9, **2**

— **W** —

Wei, S.-H.: EN+AS-ThA1, **1**
Wessel, S.: EN+AS-ThA6, **1**
Wu, H.: EN+AS-ThA7, **1**