# WORLD ENERGY FOCUS

insights from and for the WEC's global leadership community



HARSH REALITY The agenda for natural gas MARKET VOLATILITY A return to business -as-usual

A BIG STEP FORWARD ... ... for China-led development bank

### **GREEN ENCYCLICAL-**

Fix the climate, says Pope Francis



From China, the US, Brazil, Korea

> NIGERIA'S OPPORTUNITY President Buhari prioritises energy



4th International Symposium on Energy Challenges and Mechanics - working on small scales 11-13 August 2015, Aberdeen, Scotland, United Kingdom

# Why here?



#### Related Articles



- Britain faces £200bn oil loss 07 Feb 2015
- Falling oil price a curse, not a tax cut, for British economy? 27 Jan 2015
- UK's trade deficit widens to 2010 high as consumers take advantage of falling oil 06 Feb 2015
- Andrew Sentance: Inflation rise will be cost of oil price fall as spending begins 06 Feb 2015

# The Telegraph

Home	Video	News	World	Sport	Finance	Commen	t Culture	Travel	Life	Wom	en	Fa
Budget	Comp	anies	Comment	Perso	nal Finance	e   ISAs	Economy	Markets	Prop	erty 📋	Ente	rpri
HOME	FINANCE	» OIL PI	RICES									

Aberdeen is paying the price for oil's decline

Six years after the financial crisis, with the rest of Britain poised to boom, Aberdeen faces a downturn





3

"Energy Challenges and Mechanics"

Heterogeneous Electrical and Mechanical Field Effects in Functional Materials

Ken Reifsnider,<sup>1</sup> Fazel Rabbi,<sup>2</sup> Rassel Raihan,<sup>1</sup> and Vamsee Vadlamudi<sup>2</sup> 1 University of Texas Arlington, UTA Research Center 2 University of South Carolina

4th International Symposium on Energy Challenges and Mechanics - working on small scales 11-13 August 2015, Aberdeen, Scotland, United Kingdom

# Heterogeneous Mechanical and Electrical Field Effects in Functional Materials (for Energy Storage and Conversion)

#### **OUTLINE:**

- Perspectives Challenges and opportunities
- Heterogeneous materials 'universal dielectrics;' membranes as an example
- Electrical / mechanical coupling for heterogeneous materials
- "Heterogeneous Fracture Mechanics"
- Design Detect Predict

Ken Reifsnider, Univ. Texas Arlington

4th International Symposium on Energy Challenges and Mechanics - working on small scales 11-13 August 2015, Aberdeen, Scotland, United Kingdom

## Multifunctional Heterogeneous (Composite) Materials -



# **Heterogeneous Functional Materials (HeteroFoaM):** "all heterogeneous materials are fundamentally dielectric"



Ken Reifsnider, Univ. Texas Arlington

### What Should This Picture Look Like?

Including Grain Boundary/Interface Structure and Composition

### **Composite Membranes:** for: Nuclear waste management,

chemical processing, medical devices, .....



Figure 3: Proposed oxygen ionic and electronic transport paths.



(a) Traditional dual phase MIECs (DP-MIECs) without formation of the third phase. (b–d) Novel ternary phase MIECs (TP-MIECs) shown as (b) CGO–CFO5050 (c) CGO–CFO6040 and (d) CGO–CFO8020 in this work.

Enhancing grain boundary ionic conductivity in mixed ionic–electronic conductors

Ye Lin, Shumin Fang, Dong Su, Kyle S Brinkman & Fanglin Chen

Affiliations | Contributions | Corresponding authors

Nature Communications 6, Article number: 6824 | doi:10.1038/ncomms7824 Received 23 September 2014 | Accepted 03 March 2015 | Published 10 April 2015



Ken Reifsnider, U. Texas Arlington

Temperature °C

# **IONIC PHASE**

### **FLUORITE TYPE**

- Calcium fluoride (CaF<sub>2</sub>) has a fluorite crystal structure
- FCC packing of cations, with anions in all tetrahedral positions
- Also can be described as simple cubic packing of anions with cations in the cubic (8coordinate) positions

## GADOLINIUM DOPED CERIA (GDC)

- CeO<sub>2</sub> has the same atomic structure as calcium fluoride
- GDC has a structure similar to CeO<sub>2</sub>with one alternative lattice site filled with ceria and trivalent dopant gadolinium which gives rise to the creation of oxygen vacancies



# **ELECTRONIC PHASE**

#### SPINEL-TYPE MIXED-METAL COMPOSITES

- Spinel type metal oxide can be represented as AB<sub>2</sub>O<sub>4</sub> where A is a divalent such as Mg, Fe, Mn, Zn, and Cu.
- B is a trivalent atom Ti, Fe, Al, and Co.
- In a normal spinel structure, all the trivalent cations are located in half of the octahedral sites, while all of the divalent cations occupy 1/8 of the tetrahedral sites.

# COBALT FERRITE ( $CoFe_2O_4$ )

- CoFe<sub>2</sub>O<sub>4</sub> has an inverse spinel crystal structure.
- In the case of an inverse spinel such as CoFe<sub>2</sub>O<sub>4</sub>, the Co cation occupies one half of the octahedral coordination sites. Half of the Fe<sup>3+</sup> cations occupy the other half of the octahedral coordination sites as well as all of the tetrahedral coordination sites.



Crystal Structure of Cobalt Ferrite  $(CoFe_2O_4)$ 

# **SEGMENTATION**



2D image stack obtained from 3D x-ray scan (W. Chiu, UConn)



Mask segmentation of different membrane phases based on their grayscale intensity



Grayscale segmentation based on X-ray absorption behavior



Stack of segmented mask representing different layer of the membrane structure

F. Rabbi, USC

# **3D PHASE REPRESENTATION**



Three dimensional volume representation of separated constituents of 60%GDC-40%CFOa) GDC, b) CFO, c) GFO and d) pore.

Wilson Chiu, UConn; Fazle Rabbi, U. South Carolina

# **COMPUTATIONAL MODEL**

### MODEL SETUP

- Concentration gradient is applied as boundary condition on opposing faces
- Other boundaries are kept as chemically and electrically included
- Electric potential can be applied in the boundaries if required in the system
- Individual diffusion properties are applied to the phases
- Negligible contribution from internal boundary between
- Parameter dependent material properties can be used for each phases



Domain with applied boundary condition

# **TRANSPORT MODEL**

### **NERNST-PLANCK EQUATIONS**

$$N_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_i + c_i \boldsymbol{u}$$

 $N_i = Flux of species, i(mol/m^2.s)$   $D_i = Diffusion co-efficient (m^2/s)$   $c_i = Concentration of ion, i (mol/m^3)$   $z_i = valance of species$   $u_{m,i} = mobility (s/mol/kg)$  F = Faraday constant  $\phi_i = Electrolyte Potential$ u = velocity vector (m/s)

# RESULTS

#### COMPARISON

- Comparison with reported result by Lin, Y. et al.
- Initial study is with a 6040 GDC-CFO mixture
- Temperature dependent reported value
- The reported result includes grain boundary contribution to total flux



Lin, Y. et al. "Enhancing grain boundary ionic conductivity in mixed ionic–electronic conductors." Nat. Commun. 6:6824 (2015).

# **RESULTS – HOW THE MATERIAL DESIGN CONTROLS THE FUNCTIONALITY**

### $O_2$ CONCENTRATION GRADIENT

- Concentration gradient of different species is obtained from the model
- Volume plot shows concentration variation across material and boundaries
- Slice plot indicates through the thickness concentration gradients

### **SPECIES TRANSPORT PATH**

- Species transport paths show flow of two species through the phases
- This can be useful to study the effect of path variation and morphology on the overall flux transport
- Integral of transport path can be obtained to calculate ion travel distance through the membrane



Oxygen ion concentration a) volume plot, b) slice plot



Oxygen ion concentration a) volume plot, b) slice plot

# "Universal Dielectrics"



Charge displacement Capacitance in HeteroFoaM materials - some fundamental understandings:



The <u>local</u> properties, shapes, and mobilities determine the dielectric response

Ken Reifsnider, Univ. Texas Arlington

# ANALYSIS: DIELECTRIC BEHAVIOR OF COMPOSITE MATERIALS

- Embedded boundary method, closed form; representative volume element
  - Comsol Multiphysics AC/DC module was used for computational
- Maxwell's equations and continuity of charge:

 $-\nabla d((\sigma + j\omega\varepsilon_0)\nabla V - (\mathbf{J}^c + j\omega\mathbf{P})) = d\mathbf{Q}_j$ 

- with no internal current source and charge density  $-\nabla . d((\sigma + j\omega\varepsilon_0)\nabla V) = 0$ 

- Time-variable current is applied on the input port to measure impedance response.
- Frequency varied from **0.1Hz-1MHz**.
- Frequency dependent single phase material properties can be applied to corresponding material domain for each different frequency.
- Frequency dependent material properties-Obtained by NOVOCONTROL<sup>TM</sup>.



Huray P.G., (2010), Maxwell's equation, John Wiley & Sons, Inc. Hoboken, New Jersey



**A**1

0.9 0.8 0.7 0.6

0.4

0.3

Potential distributions along the line



Space charge densities along the line

# Surface charge: determined by the jump in the gradient of the potential

#### Surface Charge Density

The surface charge density on a solid is defined as the total amount of charge q per unit area A,

$$\sigma = \frac{q}{A}.$$
 (1)

The surface charge on a surface S with surface charge density  $\sigma({f r})$  is therefore given by

q

$$= \int_{S} \sigma(\mathbf{r}) \, d^3 \mathbf{r}. \tag{2}$$

In cgs, Gauss's law requires that across a boundary

$$\mathbf{E}_1 - \mathbf{E}_2 \cdot \hat{\mathbf{n}} = 4\pi\sigma,$$
 (3)

where  $\mathbf{E}_i$  is the electric field in medium *i* and  $\hat{\mathbf{n}}$  is the unit normal vector, which is equivalent to



### Surface charge: confirmation -EFM Internal

- Cantilever on first pass is at set at 75nm from sample surface and topography data is collected.
- On the second pass the cantilever is backed away and measures electrical properties







\* K. L. Reifsnider, F. Rabbi, J. Baker, J.-M. Adkins and G. Liu, Processingproperty relationships in advanced multi-functional composite materials: Management of dielectric behavior, Proc. Int. Conf. Processing and Manufacturing of Advanced Materials, 2–6 December 2013.

\* K. L. Reifsnider, Q. Liu, J.-M. Adkins, J. Baker, F. Rabbi and K. Brinkman, Relationship of micromorphology to charge storage and transfer properties in heterogeneous functioanl materials, Proc. World Conf. Computational Mechanics, 13–18 July 2012.

Fig. 15. (a) Measured surface charge density in the polarization regions on the left on the sample interface  $(+1.2e-8 \text{ C/m}^2)$ , (b) right  $(-9.66e-8 \text{ C/m}^2)$  of the circular inclusion for an applied specimen bias voltage of 10 V.



# **Physics Based Heterogeneous Non-dilute Material Models**

Consider solutions to the non-dilute problem for defect second phases with the following geometries and orientations:

 vary size → volume fraction
vector electromagnetic field applied
Systematic variation of orientation

 $-\nabla d((\sigma + j\omega\varepsilon_0)\nabla V) = 0$ 

E

Ken Reifsnider, Univ. Texas Arlington



# **Dielectric property emergence:**



Frontier Science → models/validation → material design tools & demOS

$$-\nabla d((\sigma + j\omega\varepsilon_0)\nabla V) = 0$$

Conceptual innovation: Construct design tools to predict compliance with multiphysics (mechanical and electrical) applied fields during nonconservative state changes:

New closed form, nondilute model of material state changes caused by micro-defect accumulation in heterogeneous materials predicts unexpected nonmonotonic variations.



 \* Meso-Design of heterogeneous dielectric material systems: structure property relationships, Baker, Adkins, Rabbi, Liu, Reifsnider, and Raihan, J. Advanced Dielectrics, 3#1 (2013)

\* Heterogeneous mixtures of elliptical particles: directly resolving local and global properties and responses, Q. Liu and K. Reifsnider, Journal of Computational Physics (2012), doi: http://dx.doi.org/10.1016/j.jcp.2012.09.039





A study of gadolinia-doped ceria electrolyte by electrochemical impedance spectroscopy, Zhang , Liu , Brinkman , Reifsnider , Virkar , Journal of Power Sources 247 (2014) 947-960

# Variation of real part of the permittivity with increasing volume fraction at different frequencies



24



# Concept of generalized compliance to fields (mechanical and electrical) –

# Validation:

Experiments validate global predictions of general compliance for local non-conservative material state changes caused by mechanical + electrical fields.

New tool for Material State Awareness that discriminates specific local details of damage for non-dilute accumulation of defects.



**MULTIPHYSICS DESIGN AND DEVELOPMENT OF HETEROGENEOUS FUNCTIONAL MATERIALS FOR RENEWABLE ENERGY DEVICES: THE HeteroFoaM STORY**, J. Electrochemical Society, accepted, (2013), Keynote lecture, ECS Prime, 2012 K. Reifsnider (USC), Y. Du, Wilson Chiu(UConn), Kyle Brinkman(SRNL),

Ken Reifsnider USC

Institute for Predictive Performance Methodologies

**LITA**R

UNIVERSITY OF TEXAS AT ARLINGTON

**RESEARCH INSTITUTE** 

Air Force Office of Scientific Research



# Fatigue: Physics Based Damage Models



Ken Reifsnider

# Characterization and sensor technology:

# Physics Based Damage Models for Materials State Awareness:



K. Reifsnider, P. Majumdar & P. Fazzino, "Material State Changes as a Basis for Prognosis in Aeronautical Structures," J. Aeronautical Society, Vol. 113 #1150 (2009) Silver award winner.

# Premise:

We can use dielectric state variable(s) to relate material response to mechanical and electric fields

Those state variables have the advantage of integrating and correctly interpreting the collective, emergent effect of complex damage / material state changes

The foundations of that capability are evident, rigorous, and invertable (as a foundation for design).

Institute for Predictive Performance Methodologies

RESEARCH

LITAR

UNIVERSITY OF TEXAS AT ARLINGTON



Ken Reifsnider, Univ. Texas Arlington <sup>29</sup>

# Can we demonstrate the basic foundations?

# Nonlinear deformation:

Horizontal mechanical field (ABAQUS) Vertical electrical field (COMSOL) Can we make a 1:1 association between the distinguishing features of damage development and changes in dielectric properties, e.g., capacitance?

V. Vadlamudi, U South Carolina



# Nonlinear deformation:

Horizontal mechanical field (ABAQUS) Vertical electrical field (COMSOL) Can we make a 1:1 association between the distinguishing features of damage development and changes in dielectric properties, e.g., X capacitance?



V. Vadlamudi, U South Carolina

# Nonlinear deformation:

Horizontal mechanical field (ABAQUS)



V. Vadlamudi, U South Carolina

125% Strain

# Nonlinear deformation:

Vertical (through the thickness) electrical field Internal charge accumulations interact – nonlinear results **>** can detect changes in response (slopes)



V. Vadlamudi, U South Carolina

# **Nonlinear deformation:**

# Distinctive features of nonlinear deformation revealed in capacitive response:





X



### Compression is different than tension!



V. Vadlamudi, U South Carolina







V. Vadlamudi, U South Carolina

defect types in sequence:

Horizontal mechanical field (ABAQUS)

Foundation for Predictive Methodology:

We can conduct simulations that combine predicted deformation patterns (e.g. with ABAQUS) that are directly used to predict concomitant changes in dielectric observables (e.g. with conformal models in COMSOL).



# Specific damage modes are clearly and uniquely identified



LITA/R/

 K. Reifsnider, D. Cacuci, J. Baker, J. Adkins, F. Rabbi, "Validated predictive computational methods for surface charge in heterogeneous functional materials: HeteroFoaM,<sup>™</sup> Mechanics of Advanced Materials and Modern Processes 2015, 1:3 doi:10.1186/s40759-014-0001-y

V. Vadlamudi, U South Carolina & K. Reifsnider, UTA

### DIELECTRIC CURRENT STATE ANALYSIS FOR DURABILITY PROGNOSIS AND DESIGN OF COMPOSITE MATERIALS

If we rank the initial dielectric response, then rank the break strains; we find that the <u>break strains of individual specimens predicted</u> by multiplying the average strain for all specimens by the dielectric fraction for an equal rank is an excellent estimate of strength of each specimen.

Observed



Specimen number

Rassel. Raihan & Ken Reifsnider

#### "Current State Analysis Method"

Observed and predicted values of strain to break for 20 individual specimens based on initial values of the imaginary part of the permittivity measured through the thickness of those individual specimens before load application for different input frequencies

Predicted

20

10.75 Hz

10



Institute for Predictive Performance Methodologies Predicted UTARN UNIVERSITY DE TEXAS AT ARLINGTON RESEARCH INSTITUTE Multi-Scale Design and Prognosis of Multifunctional Composite Materials: The concept -







Predict

- Multifunctional: mechanical, thermal, electrical...
- Multi-scale
- Nonlinear
- Nonconservative

- Material state: dielectric, mechanical..
- Defect state, morphology, locations
- Properties, functionality

- Performance, reliability, risk:
- Remaining strength, life, stiffness, conductivity..
- Functionality
- Risk / repair

Institute for Predictive Performance Methodologies

Ken Reifsnider, U Texas Arlington



### The authors gratefully acknowledge the support of:

- the computer simulations by NASA / EPSCoR Grant #NNX13AD43A-USC
- the broadband dielectric spectroscopy and related work from the Energy Frontier Research Center for Heterogeneous Functional Materials, the HeteroFoaM Center, under DoE Grant no.DE-SC0001061 from the Office of Basic Energy Sciences
- Laboratory and facilities support from the USC SmartState Center for Solid Oxide Fuel Cells (<u>www.sofccenter.com</u>)
- The support of the Institute for Predictive Methodologies, UTA

Ken Reifsnider, U Texas Arlington



#### **RELATED PUBLICATIONS:**

- 1. Reifsnider, K.L and Case, S., Damage tolerance and durability of material systems, John Wily and Sons, New York, 2002
- K. Reifsnider, D. Cacuci, J. Baker, J. Adkins, F. Rabbi, "Validated predictive computational methods for surface charge in heterogeneous functional materials: HeteroFoaM,<sup>™</sup> Mechanics of Advanced Materials and Modern Processes 2015, 1:3 doi:10.1186/s40759-014-0001-y
- 3. Raihan, R., Adkins, J. M., Baker, J., Rabbi, F., & Reifsnider, K. (2014). Relationship of dielectric property change to composite material state degradation. Composites Science and Technology, 105, 160-165.
- 4. K. L. Reifsnider, P. K. Majumdar and P. J. Fazzino, "Material state changes as a basis for prognosis in aeronautical structures," J. Aeronautical Society, vol. 113, no. 1150, pp. 789-798, 2009
- 5. Xing, L., Reifsnider, K. L., & Huang, X. (2009), "Progressive damage modeling for large deformation loading of composite structures," Composites Science and Technology, 69(6), 780-784.
- Raihan, R., Reifsnider, K., Cacuci, D., and Liu, Q., "Dielectric signatures and interpretive analysis for changes of state in composite materials," J. Applied Mathematics and Mechanics (ZAMM), 1–9 (2015) / DOI 10.1002/zamm.201400226
- Q. Liu and K. Reifsnider, "Heterogeneous mixtures of elliptical particles: directly resolving local and global properties and responses," Journal of Computational Physics (2012), oi.org/10.1016/j.jcp.2012. 09.039
- 8. Q. Liu, "Physalis method for heterogeneous mixtures of dielectrics and conductors: Accurately simulating one million particles using a PC," J. Comput. Phys. 230, 8256 (2011
- 9. J. Baker, J. M. Adkins, F. Rabbi, Q. Liu, K. Reifsnider and R. Raihan, "Meso-design of heterogeneous dielectric material systems: Structure property relationships," Journal Of Advanced Dielectrics, Vol. 4, No. 2 (2014), DOI:10.1142/S2010135X14500088
- 10. R. Raihan, "Dielectric Properties of Composite Materials during Damage Accumulation and Fracture," Dissertation, Mechanical Engineering, University of South Carolina, 2014
- 11. V. Vadlamudi, "Predictive Methods for End of Life Prognosis in Composites," MS thesis, Department of Mechanical Engineering, Univ. of South Carolina, 2015.

### Contributions to Conference Proceedings and Journals

- 1. Rassel Raihan, Jon-Michael Adkins, Jeffrey Baker, Fazle Rabbi, Kenneth Reifsnider; "Relationship of Dielectric Property Change to Composite Material State Degradation" Composite Science and Technology, Submitted
- 2. J. Baker, M. Haidar, R. Raihan, K. Reifsnider, "Effect of Manufacturing on the Dielectric Properties of Composite Materials." Proc. Am. Soc. Composites, U. Michigan, September, 2015
- 3. Kenneth Reifsnider, Rassel Raihan, Fazle Rabbi, and Jeff Baker; "Dielectric Current State Analysis for Durability Prognosis and Design of Composite Materials" DURACOSYS-2014, Tokyo, Japan 2014
- 4. R. Raihan, Q. Liu, K.L. Reifsnider, F. Rabbi; "Nano-Mechanics foundations and experimental methodologies for multiphysics prognosis of functional behaviour in heterogeneous functional materials (HeteroFoaM)", Procedia IUTAM (2012)
- 5. R. Raihan, K. Reifsnider, Fazle Rabbi, Jeffrey Baker, Jon-Michael Adkins, Q. Liu," A Dielectric Spectroscopy Method of Directly Assessing Composite Micro-State Evolution During Manufacturing and Deformation" Society for the Advancement of Material and Process Engineering (SAMPE), Long Beach 2013
- 6. Md Rassel Raihan, Kenneth L Reifsnider;" Generalized Compliance, A New Technique for Progressive Damage Analysis in Composite Materials" The 19th International Conference on Composite Materials, Montreal 2013
- 7. Reifsnider, K. L.; Raihan, R.; and Liu, Q.;" Rational durability design of heterogeneous functional materials: Some first principles" Mechanics of Composite Materials, 49, 31-53, (2013)
- 8. P. Majumdar, M. Raihan, K. Reifsnider and F. Rabbi, "Effect of Porous Electrode Morphology on Broadband Dielectric Characteristics of SOFOC and Methodologies for Analytical Predictions" Proc. ASME 2011 9th Fuel Cell Science Engineering and Technology, Aug. 2011
- 9. K. Reifsnider, R. Raihan, and P. Majumdar, "Durability Methodologies for Material Systems," Proc. PVP2011, July 2011



International Conference on Computational { Experimental Engineering and Sciences Institute for Predictive Performance Methodologies

