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FINAL CRADA REPORT

Date: October 1, 2009

CRADA Number: 0400401

CRADA Title: Electrochemical Oxygen Pumps

CRADA Start/End Date: February 01, 2002 to March 26, 2008

Argonne Dollars: \$148,000

Participant Dollars (in kind): \$334,000

Argonne PI: John David Carter

Industrial Partner: Praxair, Inc. World Wide Headquarters
39 Old Ridgebury Road
Danbury, CT 06810

DOE Program Manager: James Noble, Ph: 202-586-3921

Summary of Major Accomplishments:

All tasks of the Work Plan of ISTC Project #2277p have been completed, thus:

- Techniques of chemical synthesis were developed for more than ten recipes of electrolyte based on cerium oxide doped with 20 mole% of gadolinium (CeGd)O₂, doped by more than 10 oxide systems including 6 recipes in addition to the Work Plan;
- Electric conductivity and mechanical strength of CeGd specimens with additions of oxide systems were performed, two candidate materials for the electrolyte of electrochemical oxygen pump (pure CeGd and CeGd doped by 0.2 wt% of a transition metal) were chosen;
- Extended studies of mechanical strength of candidate material specimens were performed at room temperature and at 400, 600, 800 °C;
- Fixtures for determination of mechanical strength of tubes by external pressure above 40 atmospheres at temperature up to 700 °C were developed and fabricated;
- Technology of slip casting of tubes from pure (Ce,Gd)O₂ and of (Ce,Gd)O₂ doped by 0.2 wt% of a transition metal, withstanding external pressure of minimum 40 atmospheres at temperature up to 700 °C was developed. A batch of tubes was sent for testing to Argonne National Laboratory;

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- Technology of making nanopowder from pure (Ce,Gd)O₂ was developed based on chemical synthesis and laser ablation techniques. A batch of nanopowder with the weight 1 kg was sent for testing to Argonne National Laboratory;
- A business plan for establishing a company for making powders of materials for electrochemical oxygen pump was developed;
- Major results obtained within the Project were reported at international conferences and published in the Russian journal: 'Electrochemistry'.

Summary of Technology Transfer Benefits to Industry:

In accordance with the Work Plan a business trip of the following project participants was scheduled for April 22 – 29, 2006, to Tonawanda, NY, USA:

- Manager Victor Borisov;
- Leader of technology development Gennady Studenikin;
- Leader of business planning Elena Zadorozhnaya ;
- Leader of production Vasily Lepalovsky;
- Translator Vladimir Litvinov

During this trip project participants were to discuss with the project Technical Monitor J.D. Carter and representative of Praxair Inc. J. Chen the results of project activities (prospects of transition metal-doped material application in oxygen pumps), as well as the prospects of cooperation with Praxair at the meeting with the company management in the following fields:

- Deposition of thin films of oxide materials of complex composition on support by magnetron and ion sputtering, research of coatings properties;
- Development of block-type structure technology (made of porous and dense ceramics) for oxygen pump. The block-type structure is promising because when the size of electrolyte block is 2×2 inches and assembly height is 10 inches (5 blocks connected together) the area of active surface is ca. 290 \square inches (in case of 8 slots), that roughly corresponds to one tube with diameter 1 inch and height 100 inches. So performance of the system made of such blocks may be by a factor of two or three higher than that of tube-based system.

However one month before the visit, J. Chen notified us of internal changes at Praxair and the cancellation of the visit to Tonawanda, NY. During consultations with the project Technical Monitor J.D. Carter and Senior Project Manager A. Taylor a decision was made to extend the project term by 2 quarters to prepare proposals for follow-on activities during this extension (development of block-type structures made of dense and porous oxide ceramics for electrochemical oxygen pumps) using the funds that were not used for the trip to the US.

Other Information/Results: (Papers, Inventions, Software, etc.)

ELECTRIC CONDUCTIVITY OF SUB-MICRON SOLID ELECTROLYTES $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$ DEPENDING ON DENSITY AND GADOLINIUM CONTENT

Ivanov V.V.¹, Kotov Yu.A.¹, Gorelov V.P.², Borisov V.N.³, Murzakaev A.M.¹, Samatov O.M.¹, Medvedev A.I.¹, Khrustov V.R.¹, Ivin S.Yu.¹, Zayats S.V.¹, Balakireva V.B.², Sharova N.V.², Kuzmin A.V.², Vaganov E.G.², Moskalenko N.I.²

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Influence of ceramics density and composition on electric conductivity of solid electrolytes $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$ ($x = 0.09-0.31$) with sub-micron grain size ($0.1-0.3 \mu\text{m}$), prepared from nano-scale powders has been studied. Powders (surface area is 20 - 56 m^2/g) were synthesized by two different techniques: by target evaporation with pulsed CO_2 -laser and by chemical combustion technique. Ceramic specimens have been prepared by pulsed compaction technique or by quasi-isostatic (200-500 MPa) pressing and then by sintering in the air at 1100-1300°C. It has been found that electric conductivity of produced electrolytes is higher and effective activation energy of conductivity is noticeably lower than for the similar electrolytes with micron scale grains. In isothermal lines of electric conductivity of $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$ versus molar content of gadolinium ($x=0.09-0.31$) one can see the maximum that moves towards higher concentrations of gadolinium alongside with temperature growth. Density influences on conductivity of $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\delta}$ electrolytes with sub-micron grain size much stronger than it follows from simple theory of porosity that is most probably associated with specific features of grain boundaries and specific nano-scale porosity.