Materials Challenges in Alternative and Renewable Energy II

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A Collection of Papers Presented at the Materials Challenges in Alternative and Renewable Energy Conference, February 26–March 1, 2012, Clearwater, Florida

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Preface

Materials Challenges in Alternative & Renewable Energy (Energy 2012) was an important meeting and technical forum held in Clearwater, Florida, on February 26–March 1, 2012. This meeting, organized by The American Ceramic Society (ACerS), represented the third conference in a new series of inter-society meetings and exchanges, with the first of these meetings held in 2008, on "Materials Innovations in an Emerging Hydrogen Economy." The current Energy Conference- 2012 was larger in scope and content, and included 238 participants from 19 countries and included more than 200 presentations, tutorials and posters. The purpose of this meeting was to bring together leaders in materials science and energy, to facilitate information sharing on the latest developments and challenges involving materials for alternative and renewable energy sources and systems.

Three of the premier materials organizations in the U.S. combined forces with ACerS to co-sponsor this conference including ASM International, The Minerals, Metals & Materials Society (TMS), and the Society of Plastics Engineers (SPE). Between these four societies each of the materials disciplines, ceramics, metals and polymers, were represented. In addition, we were also very pleased to have the support and endorsement the Materials Research Society (MRS) and the Society for the Advancement of Material and Process Engineering (SAMPE).

Energy 2012 was highlighted by eight plenary presentations on leading energy alternatives. In addition, the conference included technical sessions addressing state-of-the art materials challenges involved with Solar, Wind, Hydropower, Geothermal, Biomass, Nuclear, Hydrogen, the Electric Grid, Materials Availability for Alternative Energy, Nanocomposites and Nanomaterials, and Batteries and Energy Storage. This meeting was designed for both scientists and engineers active in energy and materials science as well as those who were new to the field.

We are very pleased that ACerS is committed to running this materials-oriented conference in energy, every two years with other materials organizations. We believe the conference will continue to grow in importance, size, and effectiveness and provide a significant resource for the entire materials community and energy sector.

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Nuclear

STATE OF NUCLEAR ENERGY IN THE WORLD

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ABSTRACT

U.S. President Dwight D. Eisenhower's 1953 "Atoms for Peace" speech at the United Nations laid the foundation for the present global nuclear enterprise. In his speech, he recommended the creation of the International Atomic Energy Agency. He offered nuclear technology developed in the United States to other nations as part of a broad nuclear arms control initiative. Since 1953, the world has produced over 400 nuclear power reactors and all but three nations have signed the nuclear nonproliferation treaty (NPT). Significant nuclear arms control treaties have been signed. Important international organizations related to nuclear matters have been established. Perhaps the most important is that neither World War III nor nuclear conflict has occurred.

The end of the Cold War, the events of September 11, 2001, and almost global support for the resurgence of nuclear energy have created a new opportunity to reinvigorate our commitment to peace and prosperity built around a new "Global Nuclear Future." For the U.S. to return to its former position as a visionary leader in the beneficial use of nuclear technology and materials on a global scale, it is imperative that steps be taken to reverse the conditions and decisions that led to the present situation—for the most part, the U.S. nuclear supply industry has moved offshore. This will require an integrated or holistic view of the global nuclear enterprise, from the cradle-to-the grave. Some of the realities of the global nuclear state are outlined in the paper.

INTRODUCTION

The global nuclear picture is complex and changing almost daily, as illustrated by Figure 1. We first performed a global assessment in 1997 working with the U.S. Center for Strategic and International Studies.[1] While the influence of these factors has changed over the past fifteen years, we still need to use civilian nuclear energy as an arms reduction vehicle and consume significant quantities of excess nuclear materials. Reapplication of excess defense nuclear assets in several countries to open and transparent civilian nuclear services is also needed to separate defense and civilian infrastructures. Since the mid 1980's, several emerging nuclear suppliers and users have become capable of competing on the global marketplace, including China. World-wide pressures have changed the energy cost/risk picture. The price of oil in 1997 was one-tenth of what it is today. Our concerns about clandestine nuclear trade in 1997 centered mainly on the need to prevent global trade in "loose nukes" from the Former Soviet Union. Today we have a similar concern with North Korea and Iran. The end of the Cold War and growth of the EU to include former Soviet Bloc countries has resulted in new energy stresses. We still argue over whether excess nuclear weapon materials are an asset to be productively used or a liability requiring large investments in safeguards and security. In 1997, Iraq and Libya were considered the primary proliferators. Today we are equally concerned about Iran, North Korea, and terrorism and three countries remain that have not signed the nonproliferation treaty.

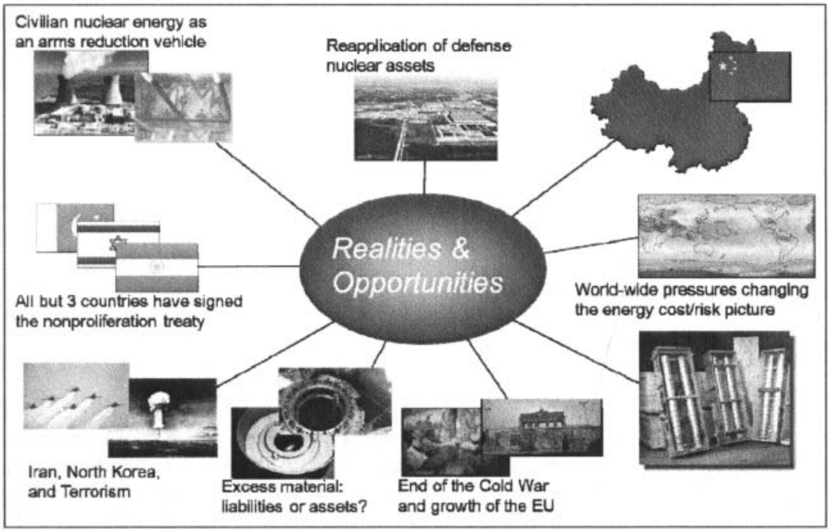

Figure 1. The Global Nuclear Picture is Complex and Changing Almost Daily

DISCUSSION

As illustrated in Figure 2, addressing our collective energy future is on the critical path to global peace and prosperity.[2,22] Energy supply and use have many ties. The prosperity of any nation depends on using energy to produce exportable goods and services. Protecting energy supplies and deliveries drives the national security strategy of many countries, including the U.S. In the "globalization trend," no market is more globalized than energy markets. However, free energy markets are disappearing as more governments decide to control the supply side.

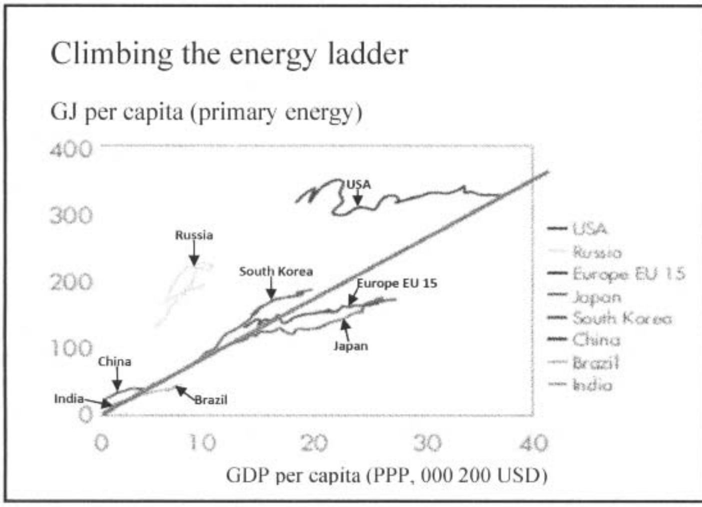

Figure 2. Climbing the Energy Ladder

From a U.S. perspective, there are two sides of the energy conundrum. Energy availability is directly tied to any nation's economic health. Developed nations like the U.S. must change their energy posture to continue to sustain and grow their own prosperity. At the same time, other nations must climb the energy ladder to achieve prosperity and reduce the stresses that lead to poverty, despair, and susceptibility to radical movements. This trend will be a hallmark of the 21st century—today's "have-nots" will demand and must have access to adequate and secure energy supplies. However, an order of magnitude increase in today's energy consumption would be needed to achieve a global minimum standard of living near that of Malaysia's by 2050. While doing so could be key to achieving global peace and prosperity, there is a huge potential for conflict over access to conventional, finite energy resources. Fifty-four percent of the world's natural gas is located in Iran and Russia and almost two-thirds of the world's oil supplies are located in the Mideast.[3,23,25] This conflict potential is directly responsible for a significant fraction of the world's defense posture and expenditures. And, as abundantly illustrated by today's economic stresses, energy scarcity slows world GDP growth (with major impacts on global economies).

Since this curve was developed, China has been "climbing the ladder" at almost a 9% growth rate. According to an article in the Washington Post in 2004,[4] China consumed ½ of the world's cement, 1/3 of the world's steel, 1/5 of the world's aluminum, and approximately 1/4 of the world's copper. China became the second largest importer of oil.[24] As China becomes much more dependent on foreign resources, it too will have to develop a naval capability to protect the pipeline to those resources.[5]

As illustrated by the impact of China's growth above, and recognizing that another two billion people have little access to energy, all forms of energy will be required to meet the global needs of this century. Fossil resources must be used and demand for access to oil and natural gas supply sources in many unstable regions of the world will continue to increase.

Another issue in the U.S. and other countries is the impact of our domestic energy mix on growing trade deficits in U.S. manufactured products.[6] The U.S. trade balance in chemical products is driven by natural gas prices. During the 1½ to 15 years between 1990 and 2005, this trade balance went from a $15B trade surplus to a $10B trade deficit.[4] "Why did this happen"—hundreds of electric-power plants (~300 GWe) built in recent years are fired by natural gas and this increase in demand has made other goods that are dependent on gas non-competitive on the global marketplace.

A single pound of low enriched uranium contains energy equivalent to 33 million cubic feet of natural gas, 250,000 gallons of gasoline, or 4 to 6 million pounds of coal.[7,8] There is no doubt that this resource will be exploited. Expanded use of nuclear energy will provide many options (and also many challenges) and we must simultaneously address nuclear proliferation concerns as we address these future energy needs. The global inventories of fissile materials has grown substantially over the last 50 years. Recent estimates of the current inventories of HEU and Pu are 64 tonnes civilian HEU, 1,475 tonnes military HEU, 200 tonnes military Pu, and 1708 tonnes of civilian Pu (19% separated). [9,21]

This amount of material could supply U.S. reactors for many years. On the other hand, this material could be used for hundreds of thousands of nuclear weapons. Therein lies the paradox and we need to solve it now—either promote and enable the peaceful use of these assets or worry about their existence forever.

Most nations using or desiring nuclear energy resources have renounced nuclear weapons and entered the Non-Proliferation Treaty. Many "so-called" threshold States of the 1980's have signed the NPT. These include South Africa—the first nation to actually disassemble a nuclear weapons stockpile—and Argentina, Brazil, Algeria, South Korea, and others. Several of these countries could become very competitive global nuclear suppliers.[10] For example Argentina has bilateral nuclear cooperation agreements with Algeria, Brazil, Peru, Romania, Turkey, Yugoslavia (Serbia), India, Italy, Iran, Israel, Pakistan, Libya, the Czech Republic, and Germany. Argentina is also developing a small standardized reactor for export to developing nations and has developed indigenous capabilities in uranium enrichment, reprocessing, reactor design, fuel design, and waste management. Other emerging supplier nations with indigenously developed capabilities include China, South Korea, Japan, Kazakhstan, Ukraine, 'Russia,' South Africa, India, and Brazil.

Nuclear fuel cycle technology and enrichment and reprocessing capabilities are widespread. If one considers the former Soviet Union nations in the "developing" category, more than one half of the world's uranium resources are in the "developing world." In fact, more than 30% of the world's uranium deposits are located in Africa.

Today, over 400 power reactors supply 17% of the world's electricity and most are in developed countries. Table 1 lists the currently operating power reactors across the globe and country-by-country plans for expansion.[11,26]

Table 1. World list of Nuclear Power Plants

Argentina – 2 operating, 1 forthcoming	Mexico – 2 operating
Armenia – 1 operating	Netherlands – 1 operating
Belgium – 7 operating	Pakistan – 3 operating, 1 forthcoming
Brazil – 2 operating, 1 forthcoming	Romania – 2 operating, 6 forthcoming
Bulgaria – 2 operating, 2 forthcoming	Russia – 33 operating, 10 forthcoming
Canada – 18 operating,	Slovakia – 4 operating, 2 forthcoming
China – 16 operating, 26 forthcoming	Slovenia – 2 operating
China (Taiwan) – 6 operating, 2 forthcoming	South Africa – 2 operating
Czech Republic – 6 operating	South Korea – 21 operating, 5 forthcoming
Finland – 4 operating, 1 forthcoming	Spain – 8 operating
France – 58 operating, 1 forthcoming	Sweden – 10 operating
Germany – 9 operating	Switzerland – 5 operating
Hungary – 4 operating	Ukraine – 15 operating, 1 forthcoming
India – 20 operating, 6 forthcoming	United Kingdom – 19 operating
Iran – 1 operating	USA – 104 operating, 1 forthcoming
Japan – 50 operating, 2 forthcoming	

As noted above, global nuclear energy expansion can create proliferation concerns. Today's (and tomorrow's) "hot spots" may see significant nuclear energy implementation throughout the 21st century. Table 2 lists the countries participating in the December 2006 IAEA meeting on global nuclear expansion.[12]

Table 2. Countries participating in December 2006 IAEA meeting on Global Nuclear Expansion

Algeria	Argentina	Australia	Bahrain
Belarus	Cameroon	Canada	Chile
China	Croatia	Czech Republic	Egypt
Finland	France	Germany	Georgia
Ghana	Greece	India	Indonesia
Islamic Republic of Iran	Japan	Jordan	Kenya
Republic of Korea	Lithuania	Malaysia	Mexico
Morocco	Namibia	Nigeria	Poland
Russian Federation	South Africa	Sudan	Syrian Arab Republic
Tanzania	Tunisia	USA	Uruguay
United Arab Emirates	Venezuela	Vietnam	Yemen

In 1953, U.S. President Dwight D. Eisenhower started the Atoms for Peace Program to address a number of U.S. national security problems:[13]

1. Increasing global competition over energy resources and a need to fuel rebuilding Europe and Japan after WWII;
2. The need to divert Soviet materials, technology, people, and infrastructure into peaceful purposes; and
3. The need to "manage" the likely spread of nuclear know-how and technology.

Nuclear energy in the U.S. has performed very well over the past few decades. However, the U.S. must meet major 21st century challenges regarding the future global nuclear enterprise; in particular, American competitiveness in the global nuclear marketplace and global nuclear weapon proliferation.

In 2004, U.S. President George Bush announced support for new measures to counter the threat of weapons of mass destruction, including a global nuclear fuel cycle model for the 21st century based on "cradle-to-grave" materials and technology partnerships.[14] Fuel suppliers would operate reactors and fuel cycle facilities, including fast reactors to transmute the actinides from spent fuel into less toxic materials. Fuel users would operate reactors, lease and return fuel, and not have to worry about disposal of radioactive materials. The IAEA would provide safeguards and fuel assurances, backed up with a reserve of nuclear fuel for states that do not pursue enrichment and reprocessing

The "supply and return" concept addresses a major potential proliferation concern with expanded use of nuclear power. Developing such a comprehensive fuel cycle service capability would provide market advantages superior to the current approach, virtually defining how nuclear trade in the 21st century will evolve and enable the nuclear powers to help the developing world acquire the energy resources necessary for achieving a prosperous future and for globally controlling environmental impacts.[15] From a global security perspective it would eliminate the need for customers of exportable nuclear systems to have enrichment and reprocessing capabilities.

Most of the emerging market opportunity across the world is for smaller reactors.[16] According to the IAEA, a small reactor is 0-300 MW(e), while a medium sized reactor generates 300-700 MW(e). Fundamentally, most countries cannot really absorb large thousand Mega watt nuclear systems. Of 435 nuclear power plants around the world last year, 138 were small and medium sized reactors (SMRs). Table 3 lists the world's operating SMRs. These reactors generated 60.3 GW(e) or 16.7% of the world nuclear electricity production. Of 31 recently constructed NPPs, 11 were SMRs.

Table 3. World's operating Small and Medium Reactors[17,27]

Developing/Transitioning Countries		
Argentina – 2	Armenia – 1	Hungary – 4
Czech Republic – 4	Slovakia – 4	Romania – 2
Slovenia – 1	Russia – 11	China – 7
Ukraine – 2	Pakistan – 2	
India – 18	Brazil – 1	
Developed Countries		
Britain – 18	Belgium – 2	Canada – 8
Finland – 2	Japan – 18	Netherlands – 1
South Korea – 6	Spain – 1	Sweden – 2
Switzerland – 3	Taiwan – 2	US – 16

According to one evaluation of the emerging world market, almost 80% of 226 countries are limited by infrastructure to small to medium sized nuclear systems. In fact, only 16% of Mexico's generating systems are greater than 250 MWe in capacity. One could argue that smaller nuclear systems also make sense in large markets such as the U.S. Since 1993, almost 300 GWe of small-to-medium sized natural gas fuel generating systems have been added to the U.S. generating capacity.[18] If smaller long-lived nuclear systems could compete with the rising and unpredictable cost of natural gas, U.S. utilities would have a "modular" capability for meeting increasing demand and for distributed non-electric applications such as oil shale development.

Large-scale development of advanced, right-sized reactors for the emerging world market is the key to enabling nuclear energy to grow as needed and exploit nuclear energy's million fold advantage in energy intensity. More than 50 concepts and designs of innovative SMRs are being developed by *Argentina, Brazil, Canada, China, Croatia, France, India, Indonesia, Italy, Japan, the Republic of Korea, Lithuania, Morocco, Russian Federation, South Africa, Turkey, USA, and Vietnam.* Most of these innovative SMRs also can provide for *non-electric applications* such as water desalination.[19]

Right-sized reactors could be sized to developing country energy grids, factory produced, fueled, sealed, and transported to the site. Some designs could result in secure, highly proliferation-resistant exportable reactors that require no refueling for up to 30 years and would enable the expansion of nuclear-based energy services to most developing countries and produce hydrogen and drinking water, in addition to electricity. These long-lived reactor concepts employ multiple approaches to coolants (H_2O, Na, Pb, Pb-Bi); spectrum characteristics (thermal, epithermal, fast); fuels (metal, particle, nitride); power outputs (1 to 300 MW_E); and specific applications (electricity, hydrogen production, district heating, desalination).

SUMMARY

The global nuclear enterprise will rapidly change over the next quarter century. The existing nuclear states must focus on the future to be able to influence the coming global challenges. The developed countries must enable the emerging world to access clean, reliable energy supplies to fuel their economies. A global nuclear services supply and return system must be created that provides the benefits of nuclear energy to all nations while eliminating any need for production of materials of nuclear proliferation concern. Partnerships among nuclear power states could establish a new paradigm for incorporating advanced manufacturing and information technologies to improve safety, reliability, security, and transparency of fuel cycle systems. Today's research will provide a longer term foundation for creating right-sized nuclear systems that are much more efficient, create 90% less waste, and enable the cradle-to-grave export of long-lived reactors to developing markets in the world. More importantly, such systems could eliminate the need for every user of nuclear technology to develop a waste repository by pursuing multi-national enterprise concepts that provide significant safety, security, economic, and nonproliferation advantages.

Nuclear energy is already an important contributor to power generation in many countries. However, its expansion is somewhat limited by continuing focus on very large generating systems. Worldwide energy demand will grow and could grow with substantial downsides without a robust global nuclear enterprise. Oil and gas will continue to dominate, will cost more, and likely cause additional conflict. Coal can contribute more, but clean coal technology will require nuclear heat to be successful. Renewable energy sources (wind, solar) must be developed but will continue to be a niche contribution. Nuclear energy must grow to fill the needs of the 21st century and additional suppliers to the global marketplace must be developed. In fact, in the absence of near-term action, the U.S. itself will become primarily a major consumer of imported nuclear goods and services with little opportunity for nuclear exports.[20] A half-century after President Eisenhower posed his vision of "Atoms for Peace," we may at last be in a position to help launch a new, "Atoms for Peace and Prosperity" program in partnership with other nations around the world. It is a vision of the future that could lead to realistic, inexpensive, long-lived energy supplies to eradicate the underlying seeds of terrorism, convert "swords into plowshares," and provide a basis for lasting peace and prosperity.

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Batteries and Energy Storage

CORRELATION BETWEEN MICROSTRUCTURE AND OXYGEN REMOVAL IN SOLID-OXIDE-FUEL-CELL-MODEL ELECTRODES $Pt(O_2)/YSZ$ AND $Pd(O_2)/YSZ$

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ABSTRACT

Platinum and Palladium films were prepared on (111) and (100) orientated yttrium-stabilized zirconia (YSZ) by pulsed laser deposition (PLD) and then subsequently annealed. These metal films are all (111) orientated, but the detailed microstructures depend on the microstructure of the YSZ. On single crystalline (111) orientated YSZ the films are single crystalline. On twin-rich YSZ(111) twin grains (accordingly with 60° grain boundaries) can be found in the films. The films on (100) orientated YSZ are polycrystalline, mostly with 30° and 60° grain boundaries. The palladium films show stronger de-wetting during annealing, but behave similar. The Pt/YSZ and Pd/YSZ systems were electrically polarised in the manner that oxygen was built-out at the metal film (= anodic polarisation). The oxygen removal during the anodic polarisation occurs mainly at the triple phase boundary, but also at the grain boundaries. In the case of metal films with twin grains, bubbles are formed within the grains. The bubbles crack and holes are built instead. In the case of other grain boundaries, these are widened due to oxygen removal. Palladium films are also oxidised during polarisation even at the surface. Accordingly, the metal films are aging during polarisation and the electrochemical behaviour is changing.

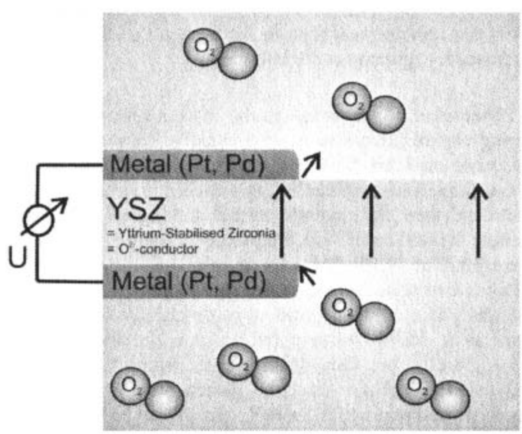

Figure 1. Electrochemical cell Pd/YSZ/Pd or Pt/YSZ/Pt, which separates a chamber into two sub-chambers of different oxygen activity.

1. INTRODUCTION

In figure 1 an electrochemical cell is shown, built by a solid system of Pt/YSZ/Pt or Pd/YSZ/Pd (YSZ = yttrium-stabilized zirconia) which separates a chamber into two sub-chambers with different oxygen activities. The sub-chamber with the higher oxygen activity works as cathode (=built-in of oxygen) and the other sub-chamber as anode (=oxygen removal). At the anode side the oxygen, which leaves the solid system, can also react with hydrogen or other gaseous reactants. Therefore, these systems are model electrodes for solid-oxide-fuel-cells or the electro catalysis. The oxygen exchange at the anode and cathode takes place mainly at the triple phase boundary between metal, YSZ and the gas phase [1-11], but Ryll et al. [3] showed, the grain boundaries within platinum are also oxygen permeable. Furthermore, Opitz and Fleig [4] found that oxygen is also stored at the Pt/YSZ interface as chemisorbed oxygen or in oxygen-filled voids. Foti et al. proposed that Pt-O type species were stored at the Pt/YSZ interface – even as a platinum oxide layer - and at the triple phase boundary [5]. In the case of palladium films such oxygen storage is more probable, since the oxygen affinity of palladium is much higher than that of platinum [6]. In figure 2 possible oxygen removal at a grain boundary and at the metal/YSZ phase boundary are illustrated.

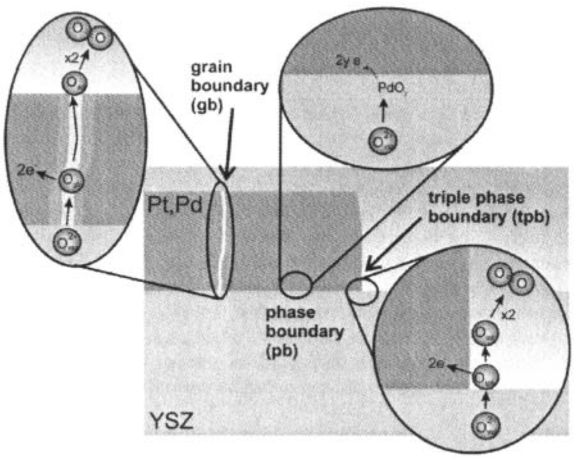

Figure 2. Supposable oxygen removal reactions in the system Pt/YSZ or Pd/YSZ at the triple-phase boundary (tpb), a grain boundary (gb) and at the interface.

Mutoro *et al.* [7] and Pöpke *et al.* [8] investigated the oxygen removal during anodic polarisation *in situ* by light and scanning electron microscopy, respectively. They found formation and cracking of oxygen bubbles within dense platinum films, but not for differently prepared porous platinum films [7]. These dense platinum films were prepared by pulsed laser deposition (PLD) of platinum on (111) orientated YSZ substrate and then subsequently annealed. Such platinum films are described to be (111) orientated and single crystalline or – in the case of a non-perfect (111) YSZ single crystal as substrate - nearly single crystalline [9,10]. Due to hole formation during anodic oxidation, the length of the triple phase boundary is extended – since within such holes the triple phase contact between the platinum, YSZ and the gas phase is given - and, accordingly, the electrode resistance is decreased. Mutoro *et al.* and Pöpke *et al.* found that favoured positions for the bubble and hole formation are close to scratches within the platinum film. Other defects within the platinum films have not been identified for preferred bubble formation. Since at defects in a crystal lattice – i.e. point defects, dislocations, grain boundaries and pores or inclusions - the crystal lattice is widened and; therefore, the energy for removing an ion or atom from a defect position is less than for removing it from a lattice