Innovation aspects and analysis in SOFCs research and development: patents sate-of-the-art

Stefan Simeonov, Maria Machkova, Vladimir Kozhukharov, Jean-Claude Grenier

Abstract: *In the last six years the SOFC technologies, research works and patent activities possess an intensive progress. The present work served an analytical overview on the current status of the SOFC patents development in USA, Japan, Germany and nine other countries. The aim is to summarize the innovating research regarding the patent branch in SOFC's development. Object of the present study are companies, universities, and institutes actively involved in the field of the SOFCs. In this context, a representative extract of more than 1050 of their patents for the period of six years (from 01.01.2005 to 30.09.2010) has been performed. Background and classification of the SOFC technology are presented as well as advantages and challenges to overcome are marked. The attention is focused mainly on the alternative compositions and advanced methods applied generally for the cathode materials (air electrode) production. In conclusion, progress and evolution priorities of the leading companies in the world, regarding SOFC technology development and innovation steps are indicated.*

Key words: *review, SOFC, IT-SOFC, innovations, patents, cathode materials, perovskites, Ruddlesden-Popper phases, nickelates.*

INTRODUTION

After almost two decades of advanced research and development, fuel cells are in their fifth round of attempt to be turned into an alternative energy source that will have commercial success. Numerous of demonstration initiatives and ongoing research and development projects into stationary applications were supported by companies and governments as well.

The military sector is also one of the key drivers for the development in the current market. In addition, several of the large automotive manufacturers are working on the use of SOFC systems for auxiliary power. Government sponsored programmes help to ensure that industry, academia and governments continue to achieve new milestones for the development of SOFC technology.

The majority of SOFC units installed across the globe are being used for small stationary applications. That includes stationary units used for domestic power supply, industrial applications requiring uninterrupted power supply (UPS) and military applications. It is interesting to see that the use of SOFC in the niche transport sector is higher than that in the large stationary category. However, companies working on SOFC for large stationary applications tend to be working on the development of hybrid technologies and use SOFC systems as part of a combination solution to power supply. In the niche transport sector the SOFC units can be used as standalone systems used as APUs to supply auxiliary power to selected vehicles including on land, marine and submarine units.

Following the world resources of SOFCs patents from universities, national research centers and companies, three main geographic splits , competitive to each other, can be defined, namely USA (North American market), Japan (Asian and Pacific markets) and Europe (United European market). In this context it is very useful to present some analytical data and information regarding the SOFC development status. A representative extract of more than 1050 patents for the period of six years (from 01.01.2005 to 30.09.2010) has been analyzed.

The aim of the present overview is to summarize the innovative investigations regarding the patent branch in the SOFCs development and applications and to analyze the tendencies of research and technology. An accent is performed over the patent status of the cathode materials for SOFCs. Objects of the review are patents from JP, US, DE and nine other countries. The patent review on the problem discussed has been accomplished via specified patent websites [1], [2].

BACKGROUND OF SOFC TECHNOLOGY

A solid oxide fuel cell is an energy conversion device that produces direct-current electricity by electrochemical reaction between a gaseous fuel (H_2) and an oxidant (O_2) across an oxide electrolyte. The key features of current SOFC technology include all solid state construction, multi-fuel capability and high temperature operation. Because of these features, the SOFC has the potential to be high-performance, clean and efficient power source and has been under development for a variety of power generation applications.

Under standard conditions, an SOFC single cell produces less than 1V output voltage. Thus, for practical applications, single cells are stacked in electrical series to build voltage system. Stacking is provided by a component as interconnect, which electrically connects the anode of one cell to the cathode of the next cell in a stack.

A SOFC single cell is a ceramic tri-layer consisting of an oxide electrolyte sandwiched between an anode and a cathode. Power is generated by the transport of oxygen ions (from air) through a ceramic electrolyte membrane where hydrogen is consumed to form water. The ceramic electrolyte membrane is sandwiched between electrodes where the power generating electrochemical reactions occur. Oxygen molecules from air are converted to oxygen ions at the air electrode (cathode), and after hoping transport across the electrolyte these oxygen ions react on the anode side with hydrogen fuel to form water as outlet product. [3]

The fuel electrode (anode) is a composite (cermet) mixture of a ceramic electrolyte material and a metal (e.g., Ni). Usually the anode material is produced as a mixture of the electrolyte material ant the oxide of the metal (e.g. NiO); prior to operation of the SOFC, the nickel oxide in the composite is reduced to a nickel metal.

One of the most common electrolyte materials is YSZ. Yttria serves the dual purpose of stabilizing zirconia in the cubic structure at low temperatures and providing oxygen vacancies [4]. The good ionic conductive electrolyte has to be non-conductor towards electrons with high density level. There are other requirements as for example a thermal expansion coefficient to be similar to the electrodes values.

PATENT CLASSIFICATIONS AND INNOVATION TENDENCIES

The patents revised are classified in the graphs below, according to several criteria. These classifications do not give exact information about the number of the patents, but served an idea for the proportions in the frames of the representative extract. The classification concerning the country of appliance illustrates the SOFC patent activities of twelve countries, leaders in the field discussed. As mentioned above North America (USA and Canada) is leading regarding the number of patents, but is ranged in second place referring to the unit installation criteria, where the leader is Europe.

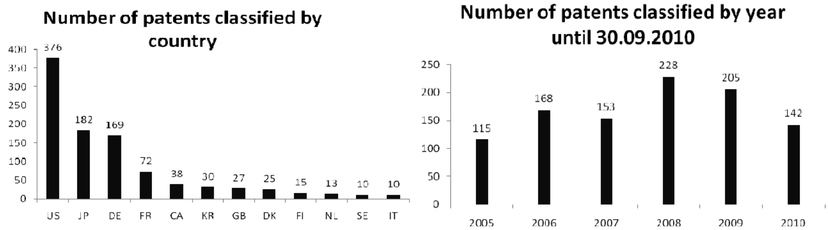

Figure 1: Classification of the analyzed patents grouping the number of the patents by a) the country of appliance and b) the year of appliance

In the last six years the development of the SOFCs revealed the possibility of patent application in all the segments of the technology as materials, systems, interconnects, etc. As the graph shows the most patents were applied in the year 2008. The few numbers less in 2009 cannot be considered for sure as a decreasing tendency, as the data for 2010 is still incomplete. All aspects of SOFC technology are active object of development in aim of achieving higher efficiency at both lower price and lower exploitation costs. One route to achieve these goals is to find constructive materials with better mechanical and electrochemical properties; another way is to optimize the work of a stack performance or an entire power unit. From the pie-graph below we can see the main directions of the SOFC innovation and technology development. The graph contains also information about another main issue that SOFC technology meets, namely the fuel production.

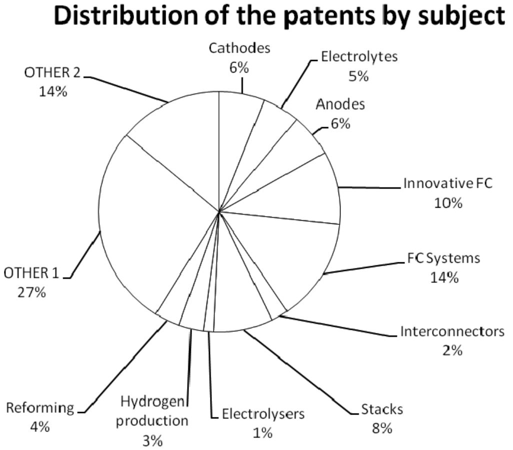

Figure 2: Pie-graph revealing the distribution of the patent by the subject; The "Other 1" and "Other 2" sectors are composed of at least ten sub-groups each

There are two sectors marked by "Other 1" and "Other 2" in high particular interest, but the detailed analysis of these sectors shows that they are composed of at least ten sub-groups each e.g. for Other 2: heat exchangers, desulfurization, sealing, vehicle application, tubular SOFCs etc. The "Other 1" sector represents patents concerning some additional to the SOFCs subjects as: fuel cartridges, start and shutdown methods of the units and many others not directly connected to the SOFC technology.

In terms of where SOFC units are installed across the globe, Europe occupies nearly 35% of the geographical split. Perhaps unsurprisingly, North America has the second largest share of the geographical split. This is a clear indication that the majority of SOFC research, development and commercialisation occurr in these two regions.

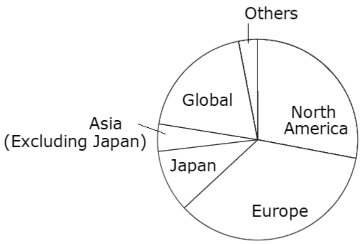

Figure 3: Pie-graph showing the proportion between the power units installed across the globe [1]

AIR ELECTRODE CURRENT STATUS

The air electrode (cathode) is a ceramic material. The majority of the cathode materials considered for SOFC application has perovskite crystal structure. The perovskite system can be generally described as having the formula ABO_3. The anion lattice of perovskite materials can be described as a three-dimensional lattice of corner sharing octahedra with the A-site cations occupying the interstitial positions between the octahedra. “Defective” perovskite structures may be achieved by substituting cations of similar radii but different valence into the A and B sites. To compensate for the charge imbalance created by the cation substitution, oxygen vacancies form in the crystal structure which is represented with δ term. In some instances, defective perovskite structures may provide enhanced electrochemical performance.

Nowadays the high operating temperatures of SOFC result on high cost and materials compatibility challenges. In this context, reducing the costs, improving the stability of performance and higher fuel efficiency are needed. The major route for achieving these objectives is the reduction of the exploitation temperature up to 700-600°C. Recently, reduction of operating temperature can be achieved either by thinning the electrolyte, or by using highly conductive electrolyte, such as doped cerias [5,6,7]. At the same time, it is important to develop a cathode material that can adapted to the intermediate temperature electrolyte and has high conductivity and low cathodic polarization at intermediate temperature so that it can reduce the power loss by ohmic resistance and cathodic polarization [3]. It has been demonstrated that reducing the thickness of electrolyte membranes lowers electrolyte resistance. This has been achieved in SOFCs with planar geometries by using porous anode as the bulk structural support, depositing a dense thin film (10μm) of the electrolyte material on the porous anode, and subsequently depositing the porous cathode (50μm). Very high SOFC power densities have been achieved at temperatures of 750 to 800ºC with planar SOFCs produced with this type of configuration. However, even better SOFC performance and lower operating temperature are expected to be achieved by using improved cathode materials [3].

One route to improve upon the aforementioned problem is to alter the materials properties, introducing oxygen ion conductivity while maintaining electronic conduction, thus making the reaction point a reaction surface. The so called Ruddlesden-Popper phase perovskite types succeed to overcome this challenges. At least one negative issue known to be associated with the use of the above-described materials is that they react with the zirconia electrolyte, forming unwanted insulating phases. Several other issues are the cost of La and that the oxygen ion conductivity is limited to less than 10% of the total conductivity. Therefore, a new and different compositional approach is warranted. [9] A specific patent scope, covering the cathode subjected patents shows a definitive direction towards finding new cathode materials with high efficiency at intermediate temperatures. Despite the significative number of patents of these new materials many intitutions continue patenting materials for the old generation high temperatures SOFCs. A key factor for this fact is the industry, where all the existing power installations are still working at relatively high temperatures. Cathodes for ITSOFC are still in the research phase but the majority of the work is more and more concentrated on this subject.

CONCLUSIONS

On the base of the patent overview the following conclusions can be extracted:

1. In the last few years the SOFC technology begins its first attempts to enter in exploitation as efficient, clean and high performing energy source.
2. A significant part of the research activities is no longer orientated to the construction of the SOFC utilities, but to optimization of its work or increasing the scale of energy production, which gives enormous field for complementary investigations, research and patents

3. The European community manifests its will to invest resources into clean energy production, with most installed SOFC units.

4. The research activities are still working on innovations mainly trying to turn the SOFCs a progressive technology, but also competitive to the present technologies.

5. The searching for routes to lower the price and the exploitation costs of the units has already obtained answers and has its directions to follow. Lower prices can be achieved by using new construction materials (electrolyte and cathode materials) as shown in the classification above the research of each one of the constructing materials is equally distributed (5-6% for the cathode, the anode and the electrolyte).

6. The planar design of the fuel cells has proven its advantages, and in the last years there are very few investigations with other types of fuel cells. As Kozhukharov reported in the beginning of this decade the planar and the tubular design were equally tested. [10]

7. The most important companies with higher level of innovations can be marked as follows: Honda Motor Co Ltd, Energy GMBH, Corning incorporated, Bloom Energy Corporation, Societe BIC, Forschungszentrum Julich GMBH, Ultracell Corporation etc.

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*nearly 1050 patents were analyzed in the frames of this review, in which the most part are marked only as numbers in the graphs

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