



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Technological forecasting of hydrogen storage materials using patent indicators

Lucas Faccioni Chanchetti ^{a,b,*}, Sergio Manuel Oviedo Diaz ^{a,b},
Douglas Henrique Milanez ^b, Daniel Rodrigo Leiva ^{a,b},
Leandro Innocentini Lopes de Faria ^{b,c}, Tomaz Toshimi Ishikawa ^a

^a Postgraduation Program in Materials Science and Engineering (PPGCEM), Materials Engineering Department (DEMa), Federal University of Sao Carlos (UFSCar), Rod. Washington Luiz, KM 235, 13565-905, Sao Carlos, SP, Brazil

^b Center for Technological Information in Materials (NIT-Materiais), Materials Engineering Department (DEMa), Federal University of Sao Carlos (UFSCar), Rod. Washington Luiz, KM 235, 13565-905, Sao Carlos, SP, Brazil

^c Information Sciences Department (DCI), Federal University of Sao Carlos (UFSCar), Rod. Washington Luiz, KM 235, 13565-905, Sao Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 14 April 2016

Received in revised form

8 August 2016

Accepted 21 August 2016

Available online 10 September 2016

Keywords:

Hydrogen storage

Technological forecasting

Bibliometrics

Patent analysis

Science and technology indicators

ABSTRACT

Hydrogen is a promising future energy carrier due to its high energetic content and sustainable appeal when produced via clean manufacturing processes. One of the technological challenges concerns its storage in a safe, compact, low mass and high gravimetric capacity manner. In this sense, many Hydrogen Storage Materials (HSM) have been investigated to house this source of energy, such as Simple Hydrides, Borohydrides, Metal-Organic Frameworks (MOFs), Alanates, AB5 Alloys, Ammonia Borane, Carbon Nanotubes and Graphene. Scientific advances aside, less attention has been paid in establishing a panorama of the technological developments in HSM. To assess the technological advances in HSM, patent analysis can be carried out using bibliometrics and text mining approaches in order to forecast the future trend of development and the main players involved in this process. In this work, we evaluated the technological life cycle stage, HSM class prominence and the role of different countries in HSM patenting. The results show that overall HSM patenting decreased after 2007, except in the case of China. On the other hand, the USA, Japan, China and the European Union (EU) were the main patenting territories. Simple Hydrides and Borohydrides were the main classes of HSM that received more attention from the USA and the EU, while Japan had a high share in Solid Solution Alloys. The life cycle stage of HSM seems to be between the first prototype market experiences and full market deployment, even though future assessment is needed to fine-tune the analysis. The developed indicators may also support the funding of new projects and decision making.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author. Postgraduation Program in Materials Science and Engineering (PPGCEM), Materials Engineering Department (DEMa), Federal University of Sao Carlos (UFSCar), Rod. Washington Luiz, KM 235, 13565-905, Sao Carlos, SP, Brazil.

E-mail addresses: lfaccioni@terra.com.br, chanchetti@ufscar.br (L.F. Chanchetti).

<http://dx.doi.org/10.1016/j.ijhydene.2016.08.137>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen is considered a promising energy carrier for the future, due to its abundance, high energy content (142 MJ/kg) and its ability to be employed both in fuel cells and combustion engines, in stationary or mobile applications, potentially producing only H₂O as an environmentally benign by-product. Hydrogen can also be generated from water using renewable energy in a sustainable closed-cycle [1]. Nevertheless, the wider use of hydrogen energy still depends on the overcoming of technological challenges, in particular, the development of safe and effective hydrogen storage technologies, since the more traditional high pressure or liquefied H₂ storage methods require high capital costs and raise safety concerns, as well as having low gravimetric and volumetric storage capacities [2].

Solid-state hydrogen storage in Hydrogen Storage Materials (HSM¹) has been extensively investigated in recent years [3]. Different attributes must be evaluated during the development and selection of HSM, such as the gravimetric and volumetric hydrogen capacities, its ease of activation (first hydrogenation), reversibility and cyclability, recyclability, toxicity, the cost of the raw materials and processing, and the temperature and pressure operation ranges. Several materials classes are being considered for hydrogen storage solutions both for mobile and stationary applications [4]. Table 1 presents the storage materials classes considered in this study, with example materials and typical operating conditions. The classes are: Simple Hydrides, AB₅ Alloys, BCC Solid Solution Alloys, AB Alloys, AB₂ Alloys [5], Borohydrides, Alanates, Amides [6], Nitrogen-Boron Compounds (N-B² Compounds) [7], Carbon Nanotubes, Activated Carbon, Carbon Nanofibers, Fullerene, Graphene [8], Metal-Organic Frameworks (MOFs) [9] and Zeolites [10].

Although several types of HSM have been investigated, none of them possess an ideal set of properties for all applications. Therefore, niche applications are being developed taking advantage of the strong points of the individual classes. For example, vehicular applications require the storage materials to be lightweight, since they implicate in extra curb weight, and the use of off-site regeneration of cartridges in chemical plants is feasible. For stationary grid storage applications, the weight of the system is less important. However, they require excellent reversibility, since the off-site regeneration is not feasible, and the cost per kWh of storage capacity must be low, since the amount of energy to be stored is very high [3].

Technological advances in HSM can be tracked using Science and Technology (S&T) Indicators. According to Moed, Glänzel and Schmoch [16], these quantitative indicators aim at supporting S&T policies by monitoring the output of research and development (R&D). Moguee [17] argues that these indicators may update the technological advances for companies and increase the security of business investments. S&T indicators are elaborated employing concepts, tools and

procedures researched in Bibliometrics, which is a discipline that quantifies registered communications, such as scientific articles, technical reports and patent documents. Recent advances in Bibliometrics include the use of information from non-structured text, such as the title, abstract, and manuscript *corpus*. This process is called ‘Text Mining’ and it extracts specific and relevant terms that can be used to develop content-oriented indicators [18]. For instance, a mined term ‘MgH₂’ in the title or abstract of a document may be used to relate it to a specific material class, e.g., Simple Metal Hydrides.

Patent documents constitute an important source of technological information, since they contain detailed descriptions of inventions and are used by patent assignees to request the exclusive rights to commercial exploitation [17]. Patent documents constitute a rich source of technical and business information, and their use can provide high-value information, for example, detailing which companies and institutes are investing in which technologies and to what extent, and thus supporting the assessment of technological life cycles and policies of countries and companies in specific technological developments [17,19,20].

The use of patent document information is, however, not uncontroversial, and some characteristics must be taken into consideration [17,21]:

- The legal framework, filing procedures and patenting culture varies among different countries
- Patents are not only filed for registering inventions. Given their legal value, they become strategic assets for potential market reservation and commercial blocking, among other uses. And especially in research, they may merely be a way of turning research results into a tangible output.
- Patents do not cover all inventions. Technologies may be maintained as industrial secrets, for example.
- After their deposit, patent documents remain confidential for 18 months. Furthermore, with third party databases, there is an indexing delay, and not all patent documents may be indexed.
- The propensity to patent varies among different areas, although it may be assumed homogeneous within a single area.
- In patent counting, the same weight is given to each document, regardless of, for example, economic value, unless a specific methodology is applied.

Nevertheless, patent-based indicators are extensively used by enterprises and entities such as the Organization for Economic Co-operation and Development (OECD³) [22] and the United States National Science Foundation (NSF) [23], indicating their high value.

The life cycle of technologies is considered to typically follow an S-curve type of development, and is divided into four stages, as shown in Fig. 1 [21]. The emergence stage is characterized by the first market trials and prototypes. Technological progress tends to be slow, as the complete understanding of the fundamentals is still in progress. The

¹ HSM: Hydrogen Storage Materials.

² N-B Compounds: Nitrogen-Boron Compounds (e.g. Ammonia Borane).

³ OECD: Organization for Economic Co-operation and Development.

Table 1 – Hydrogen storage classes.

HSM classes (this work)	Example material, capacity, operation conditions	Comments
AB Alloys	TiFeH _{1.8} ; 1,9 wt%; 5 bar, 303 K [5]	Intermetallic alloys classes are classified according to their crystalline structure. They are composed of an element A, which forms a stable simple hydride, and an element B, that forms an unstable simple hydride. The hydrogen absorption occurs through surface adsorption, followed by dissociation and interstitial diffusion [11].
AB2 Alloys	ZrV ₂ H _{5.5} ; 3 wt%; 2 bar, 323 K [5]	
AB5 Alloys	LaNi ₅ H ₆ ; 1,4 wt%; 2 bar, 298 K [5]	
BCC Solid Solutions	TiVH _{4.7} ; 2,6 wt%; 1 bar, 298 K [5]	
Alanates	LiAlH ₄ ; 7,9 wt%; up to 420–470 K [6]	Complex hydrides classes comprise compounds formed by a metallic cation and an anionic complex containing hydrogen. They generally have high capacities but also high hydrogen binding energies, implicating in high operation temperatures and often needing ex-situ regeneration [6]
Amides	Mg(NH ₂) ₂ ; 7,4 wt% (with MgH ₂) [6]	
Borohydrides	NaBH ₄ ; 10,8 wt% by hydrolysis [6]	
N-B Compounds	NH ₃ BH ₃ ; 9,1 wt% by hydrolysis [7]	Ammonia Borane is 19.6 wt% hydrogen and operates in the 150 °C region. However, it undergoes only partial desorption. The reaction kinetics with hydrogen are generally slow, and ammonia, a fuel cell poison, may be released during desorption [12]
C-Based	Activated carbon; 5 wt%; 20 bar, 77 K [13]	Storage of hydrogen in Carbon based materials, Zeolites and MOFs occurs via adsorption in the internal surfaces, without rupture of the H-H bond of the H ₂ molecule. Their storage properties depend on their specific surface area (m ² /g), pore volumes, temperature and pressure [14].
MOFs	Zn ₄ O(BDC) ₃ ; 7,1 wt%; 40 bar; 77 K [9]	
Zeolites	ZEO-Na-LEV; 2,07 wt%; 16 bar, 77 K [10]	
Simple Hydrides	MgH ₂ ; 7,6 wt%; 1 bar, 573 K [5]	Simple hydrides can be classified in ionic, covalent or metallic hydrides, according to the nature of the metal–hydrogen bond. Storage properties vary greatly with composition [15]

consolidation stage is characterized by increasing performance returns per unit of value invested, as a better understanding of the fundamentals is achieved. Product development is based on the experiences of the first stage, addressing the observed issues. The market penetration stage is when the technology finally reaches a significant portion of the potential market. In this stage, each performance increment demands higher investments, as the technology approaches its full potential. In the final stage, maturity, most of the market potential is being explored. Even small performance increments demand high investments, as the potential of the technology tends to saturate. After this stage, the technology may become a base technology (e.g. carbon steels), or descend into obsolescence, as it is substituted by new and improved solutions.

The S-curve approach, however, considers only technological development factors [21]. Actual deployment of a technology may also depend on economic and sociological

factors. These are especially important for radical innovation, as economies of scale, lock-in effects, lobbying, among others, may hinder the adoption of new technologies. A common dynamics for radical innovation are waiting games (the “chicken and egg” problem) [24]. As a hypothetical example: Since there is little hydrogen infrastructure, hydrogen car sales will potentially be low. And since there are few hydrogen cars, there is little incentive to build the hydrogen infrastructure.

For some technologies, we may also encounter a hype cycle type of development [25,26]. In this case, during the initial stages of technological development, bold claims are made about the technological potential, often amplified by media coverage, generating a peak of inflated expectations. As the technological development turns out slower than the original inflated claims, a disappointment phase takes hold, again with media hype, but this time negatively. The hype cycle is a superposition of a hype-disappointment bell-shaped curve of

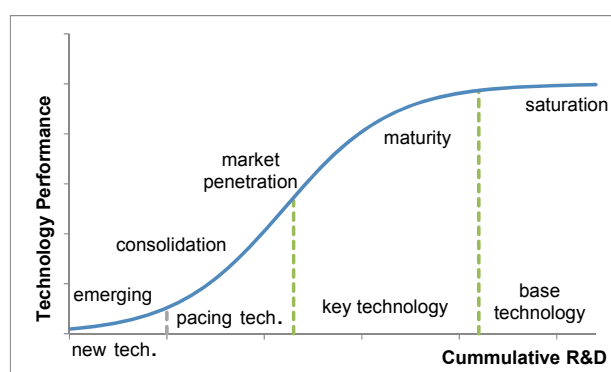


Fig. 1 – The S-curve for technological development. Source: Ernst [21].

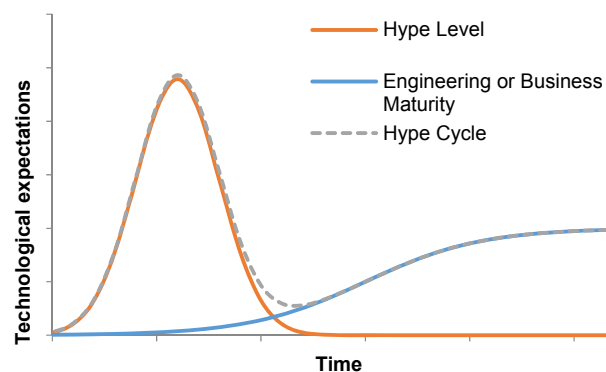


Fig. 2 – The hype cycle for technological development. Source: Steinert, Leifer [26].

Table 2 – Search expression employed for HSM Patent Document retrieval.^a

TS=((hydrogen-stor* OR stor*-of-hydrogen OR h2-stor* OR stor*-of-h2) OR (hydrogen-absor* OR absor*-of-hydrogen OR absor*-hydrogen OR h2-absor* OR absor*-of-h2 OR \ "absor* of h(2)\ ") OR (hydrogen-adsor* OR adsor*-of-hydrogen OR adsor*-hydrogen OR h2-adsor* OR adsor*-of-h2 OR \ "adsor* of h(2)\ ") OR (hydrogen-sorption OR sorption-of-hydrogen OR h2-sorption OR sorption-of-h2)] OR IP=C01B-006* NOT [TS=(batter* NOT fuel*) OR IP=A61K*)

^a The search field TS seeks key terms in the title and abstracts of bibliographic records, while IP searches records by their International Patent Classification (IPC).

expectations with the S-curve of actual technological development, as shown in Fig. 2 [26]. A recent example of hype cycle type of development are technologies related to the Human Genome Project [27].

Although from an initial point of view, hype cycles may seem negative, they constitute useful tools for breaking out of technological waiting games and triggering innovation races [24].

Previous patent analyses studies in the field have been identified. Bakker (2010) [28] analyzed patent applications for different storage technologies from car manufacturers: gaseous storage, liquefied hydrogen, metal hydrides, carbon and on-board reforming, concluding that neither was dominant and, therefore, preferred. Shih and Yen [29] depicted the evolution of patent applications, main companies and main inventors for hydrogen storage technologies in Taiwan. Chen et al. [30] analyzed fuel cell technologies patents by extrapolation of logistic curves, concluding that they are mature technologies.

In this study, we aimed at mapping and evaluating the stage of development of individual HSM technologies using patent indicators and text mining techniques, in order to obtain a panorama of the technological development of the different HSM choices, with an end to gaining insights and helping in planning and decision making in the HSM field. The time evolution, technological life cycle stage and role of countries were assessed, as well as the prominence of each HSM class. The results were elaborated into graphical technological indicators and their analysis is presented.

Materials and methods

Procedure for retrieving HSM patent data

Technological indicators were developed using bibliographic data of patent documents indexed in the Derwent Innovations Index (DII⁴) database. The patent document retrieval procedure comprises two main steps. First, we retrieved general hydrogen storage patents applying the search expression presented in Table 2.

This search expression combines general hydrogen storage key terms with the International Patent Classification (IPC⁵) code for metallic hydrides (C01B-006) [31]. We filtered documents concerning Ni-MH batteries and health-related inventions (IPC A61K), which were not associated with the goal of this study. We chose the Derwent Innovations Index (DII)

database since it covers more than 40 patent offices, and consolidates patent families⁶ into single records. Moreover, DII improves the retrieval process by allowing the use of complex Boolean search and enhancing the titles and abstracts of the indexed bibliographic records with information from the full text patent document [32]. A total of 11,260 bibliographic records of patent documents were collected in September, 2015.

The second retrieval step consisted in limiting the analysis to materials-based hydrogen storage. To achieve this goal, we imported the retrieved documents in VantagePoint (v. 7.0) text-mining software [33], separating the Titles, Abstracts and Technological Focus fields in short Noun-Phrases using Natural Language Processing available in the software. We compared these phrases with a list of terms related to Hydrogen Storage Materials Classes proposed by Chanchetti [3] and expanded in this study. This list comprises the following HSM classes: Simple Hydrates, Borohydrides, Complex Magnesium Hydrides, AB alloys, AB₂ alloys, AB₅ alloys, Solid Solution Alloys, Alanates, Zeolites, Metal Organic Frameworks (MOFs), Carbon Nanotubes, Fullerenes, Graphene, Carbon Nanofibers, Nitrogen-Boron Compounds and Amides. Finally, a total of 2026 records were obtained in the timespan from 1994 to 2013.

Elaboration and analysis of technological indicators

Technological developments of HSM were assessed quantitatively according to the guidelines and procedures recommended by the OECD Patent Statistic Manual [22] and by seminal studies in the field of quantitative analysis [16,17]. The analysis of the compiled indicators also took into account technical documents and official reports. The text-mining software VantagePoint [33] supported the process of creating frequency distribution lists of priority filing years, priority countries, and relevant noun-phrases associated to HSM. We divided the patent documents in five periods: 1994–1997, 1998–2001, 2002–2005, 2006–2009 and 2010–2012. We assessed the worldwide number of patent applications for these periods and their distribution by priority countries.

Triadic patents⁷ are considered to have higher economic value, since it is assumed that their higher cost of protection is worthwhile (although there is a possibility of a home advantage bias) [22]. Therefore, we also elaborated indicators of

⁶ A patent family comprises patent documents filed in different countries referring to the same invention. A patent document may concern a deposited or a granted patent [50].

⁷ Triadic patents are patent families with at least one USPTO patent number, one EPO patent number and one JPO patent number concerning the same invention.

⁴ DII: Derwent Innovations Index.

⁵ IPC: International Patent Classification.

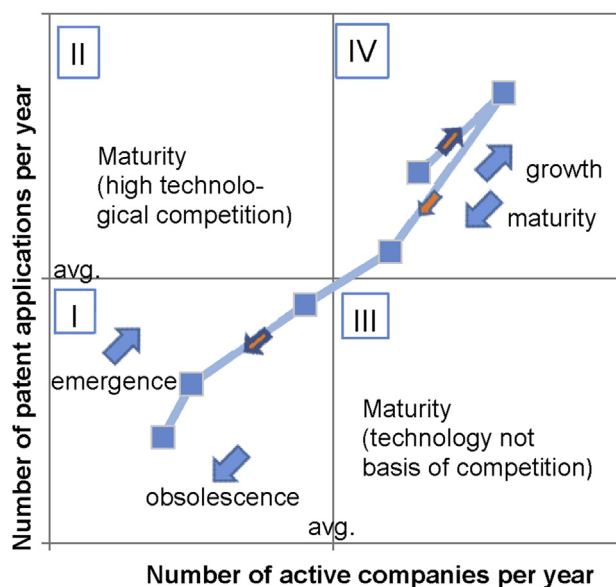


Fig. 3 – Technological life cycle assesment framework.
Source: Mogee [17].

temporal evolution, country distribution and material class distribution for triadic patents.

The HSM co-occurrence patent network analysis was performed with support of Gephi [34] software by applying its Modularity Algorithm [35]. This algorithm approximates strongly connected classes in order to reveal clusters.

Life cycle assessment

Two approaches have been applied for assessing the technological life cycle stage of HSM. The first, proposed by Campbell [36] and developed by Mogee [17], hypothesizes that the evolution of the number of patent applications versus the number of active companies in the field, taken year-by-year, can reveal the technological life cycle stage (Fig. 3). The graph is divided in four quadrants by the average number of active companies per year and the average number of patent deposits per year in the analyzed period. Quadrant I characterizes the emergence or obsolescence of the technology, depending on the direction of migration. Quadrant IV comprises key technologies, in process of growth or maturity, depending on the direction of migration. Quadrant III with many companies and few patents, characterizes a maturity stage where the technology analyzed is not the basis for competition. Quadrant II characterizes a maturity stage where the technology or product is concentrated in few companies, but the technological competition is high. However, the “correct” value for the averages can only be taken in hindsight.

The second approach, proposed by Ernst [21], hypothesizes that patterns in the time evolution of the number of patent applications can be correlated to the life cycle stages, as shown in Fig. 4. The emergence stage is characterized by a growing number of patents, with an upward inflection somewhere in the stage. The consolidation stage is characterized by a decrease or a deceleration in the number of patent applications. The market penetration stage shows a sharp

peak in the number of patent applications, which starts to fall as the technology reaches maturity.

One must however consider that the number of patent applications may follow the expectations curve of the hype cycle. In this case, it is expected that the patents have a more “market reserve” characteristic, than describing actual technological developments.

Results and discussion

Overall patent trend for HSM

The worldwide number of HSM patent documents increased rapidly in the initial periods, peaked in the 2006–2009 interval, and decreased in the 2010–2013 period, as shown in Fig. 5. In fact, HSM technology developments experienced a steep increase in the late 90's and early 2000's. Japan pioneered research funding through its “New Sunshine Plan” [37] and this might be related to its leadership in the patent filings until 2005, as shown in Fig. 6. The USA led patenting in the 2006–2009 period, with initiatives such as the 1.2 Billion US\$ “Hydrogen Fuel Initiative” [38] and the FreedomCAR program [39] driving technological developments in this period. The EU also launched similar initiatives to promote developments in this area throughout these periods [40], and this might have stimulated patent applications in that region. Korea also has important players and followed the worldwide trend. Moreover, China has been continuously increasing its number of documents in all periods and reached the leading position in 2010–2013.

In spite of China's leadership, this country filed no triadic patents in the whole period, which raises questions concerning the economic value of HSM technologies developed there, as shown in Fig. 7. Literature studies [41,42] demonstrate that subsidy patenting programs by the Chinese and regional governments are greatly responsible for the observed surge in patenting, especially for universities and research institutes, where patent applications can be important for career and promotion, without much concern for their use or economic value. The steep increase in patenting is thus not accompanied by a similar increase in patent quality.

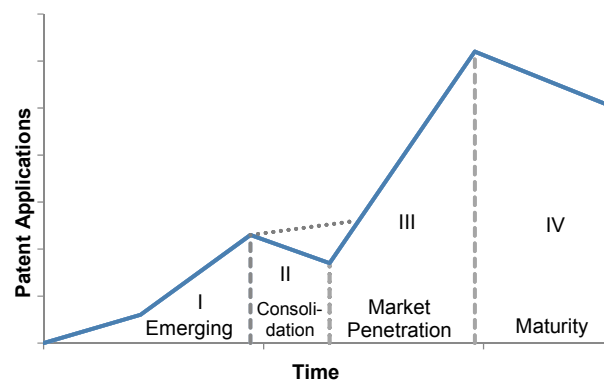


Fig. 4 – Number of patent applications along the different stages of the technological life cycle. Source: Ernst [21].

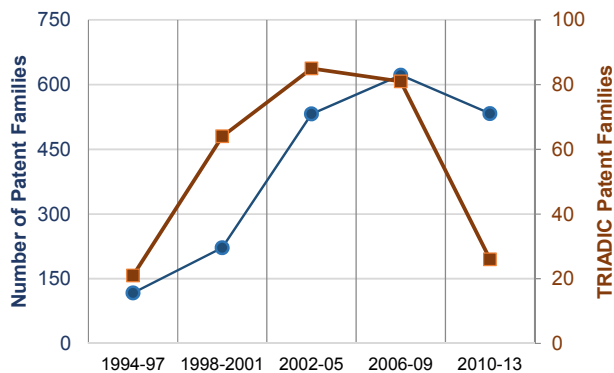


Fig. 5 – Time evolution for four-year periods of patenting for hydrogen storage materials, for total and triadic-only deposits.

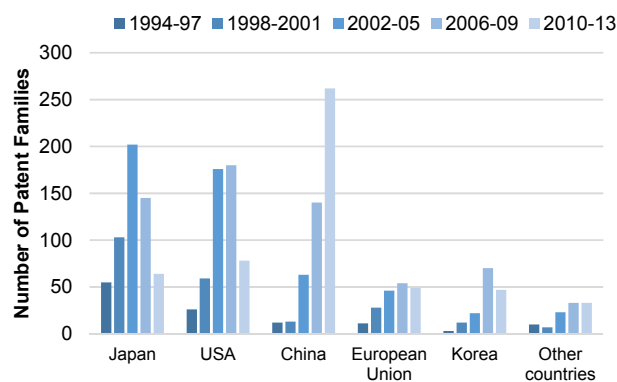


Fig. 6 – Geographical distribution and time evolution of patenting activity in HSM for selected territories.

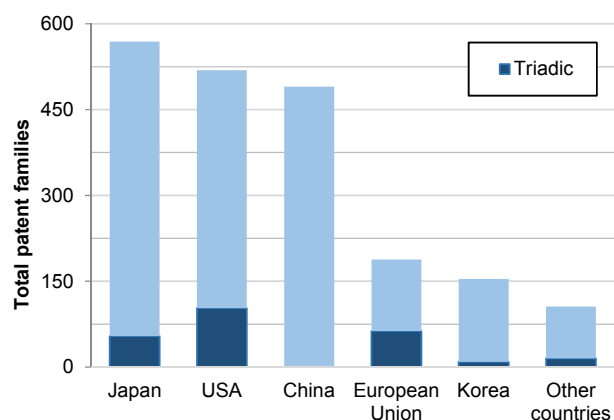


Fig. 7 – Number of HSM patent families per priority territory including triadic families.

Although Japan filed more patents than the other countries, the European Union and the USA had more triadic patents in the period, which may indicate that firms from these countries are highly interested in protecting their inventions in different markets [22].

It is worth noting that Russia filed 31 patents and India 4 in the whole period, none of which are triadic.

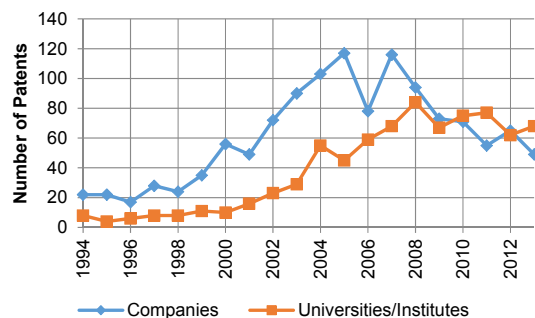


Fig. 8 – Comparison of patent applications from companies and universities/research institutes.

Fig. 6 also highlights a recent decrease in American, Japanese, European and Korean patents, which coincides with a reduction of technological development incentives [43]. Bakker (2010) [44] argued that Hydrogen Energy experienced a technological hype cycle, in which expectations in the technological development peaked at around 2002, followed by a disappointment phase at the end of the decade, as the development of the technology turned out to be slower than originally foreseen. The 2009 interview with US Secretary of Energy Steven Chu corroborated this view with his “hydrogen needs four miracles, saints only need three” quote, referring to the technological challenges in the production, distribution and storage of hydrogen and in fuel cell development [45]. Despite Chu's statement, he reconsidered his point of view in 2012, due to the abundance in natural gas made possible by fracking [46]. Starting in 2015, one of the world's largest automakers, Toyota, has been actively marketing a hydrogen fuel cell car [47], even though it uses high pressure gaseous storage and not HSM. Nevertheless, we have so far not seen a new rise in HSM patents up to the publication date of this article.

Fig. 8 shows the distribution of patents among companies and research institutions. After 2009, the number of patents from research institutions exceeded that of companies, indicating that the field possibly still requires more advances in basic research.

The analysis of the HSM technological life cycle by the Mogee framework, as shown in Fig. 9, suggests that the developments are migrating to the maturity/obsolescence region [17]. However, one may also claim that the future of HSM is uncertain, due to the fact that the last point is close to the center of the graph, so that the technology may still migrate to any quadrant. Alternatively, Ernst [21] argues that a reduction in patenting is expected in the Consolidation Phase of the technology life cycle, after the Emerging Technology stage, with the first marketing experiences driving the patenting (Figs. 4 and 5).

On the other hand, the initial surge in patenting followed by a steep decrease is consistent with a hype cycle, as proposed by Bakker (2012) [24]. In this model, the initial period is marked by a peak of inflated expectations that characterizes the hype, followed by the Trough of Disillusionment, where the expectations become driven by the actual pace of technological advance rather than by the hype (Fig. 2). Further evidence for this case resides in the fact that scientific

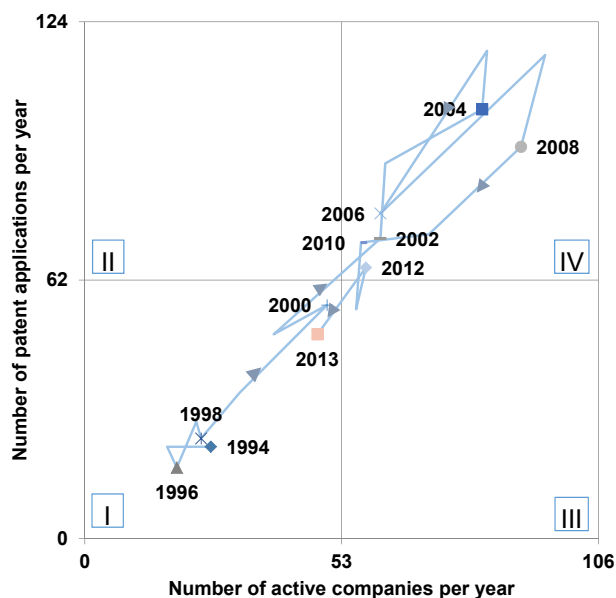


Fig. 9 – Technological life cycle assesment for hydrogen storage materials by the Mogee framework.

productivity in the area has been increasing continuously [3]. The first startups for stationary hydrogen storage in materials were founded in around 2010 [48,49], and the first commercial-scale hydrogen vehicle sales started in 2015.

Technological developments on HSM classes

Fig. 10 depicts the total number of patent documents (worldwide and triadic) for each HSM class. Much effort has been applied in developing technologies of Simple Hydrides and Borohydrides. As a consequence, they accumulated a high number of patent applications in the worldwide and triadic perspectives. Moreover, both presented a trend of constant increase in their patenting, according to Fig. 11, despite the decrease observed in the last period of the analysis for the

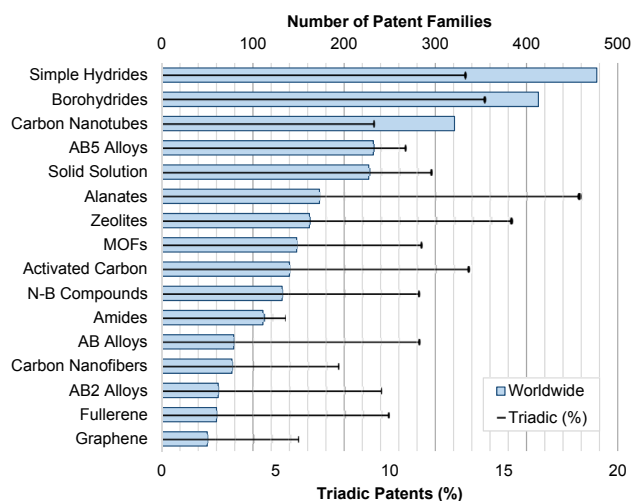


Fig. 10 – Total patenting activity and percentage of triadic patents per HSM class.

general field. Technologies associated to Alanates and Zeolites have also been the object of valuable developments, even though their number of patent applications decreased recently. In the case of carbon nanotubes, despite the high number of patent documents, a low percentage are triadic. Furthermore, the patenting on Carbon Nanotubes peaked in 2002–2005 and suffered a steep decline, which, along with weak reported performance figures [13], indicates signs of abandonment.

Simple hydrides show a trend similar to that of the general field, peaking in 2006–2009 and declining slightly in 2010–2013, according to Fig. 11. Borohydrides display steady growth, reaching leadership in the most recent period. The recent growth in AB5 is explained by the recent growth of Chinese patents (Fig. 6).

It is usual for a single patent document to claim two or more HSM classes as a consequence of their proximity to solving the technical problem (i.e. hydrogen storage). Fig. 12 shows the proximity of HSM technologies, in which three clusters were highlighted, since they share a similar concept of how to store hydrogen. The first one includes Interstitial HSM, whose main representative classes are AB5 alloys and Solid Solution Alloys. The second cluster refers to High Capacity HSM, whose main classes are Simple Hydrides and Borohydrides; and the adsorption-based Storage Cluster, whose main class is Carbon Nanotubes.

High capacity HSM was the main cluster with 44% of the total of 2026 patent documents analyzed. Simple Hydrides and Borohydrides were the main classes of this cluster, being associated to 53% and 46% of the cluster's patents, respectively. The second cluster comprised adsorption-based HSM in which carbon nanotubes is the most representative class from the group (42%). Finally, interstitial HSM constituted 24% of the sample. AB5 alloys and solid solutions were the main classes of materials in this cluster with 48% and 47% share in the cluster.

Due to their higher assumed economic value, analysis of triadic patents permits an extrapolation of possible future technological prominence of territories in specific classes. Fig. 13 shows the distribution of each triadic patents class throughout the priority territories. To illustrate, Japan has 4 and South Korea has 2 triadic patents in AB2.

Among the main HSM classes, Simple Hydrides show equilibrium between the USA and the EU, with 23 triadic patents each. Borohydrides are clearly dominated by the USA. In Alanates, the USA and EU lead with 14 and 11 triadic patents, respectively. Japan is highly prominent in Solid Solutions, and AB5 shows a progressively higher share from the EU to Japan to the USA, although without dominance.

Conclusions

There was a significant reduction in HSM patenting in recent years, with the exception of China. While this could be a sign of technological abandonment, a reduction in patenting is expected in the Consolidation Stage of the technological life cycle. This decrease may also be related to a technological hype cycle disappointment phase, where the initial inflated expectations of the hype phase converge with the actual

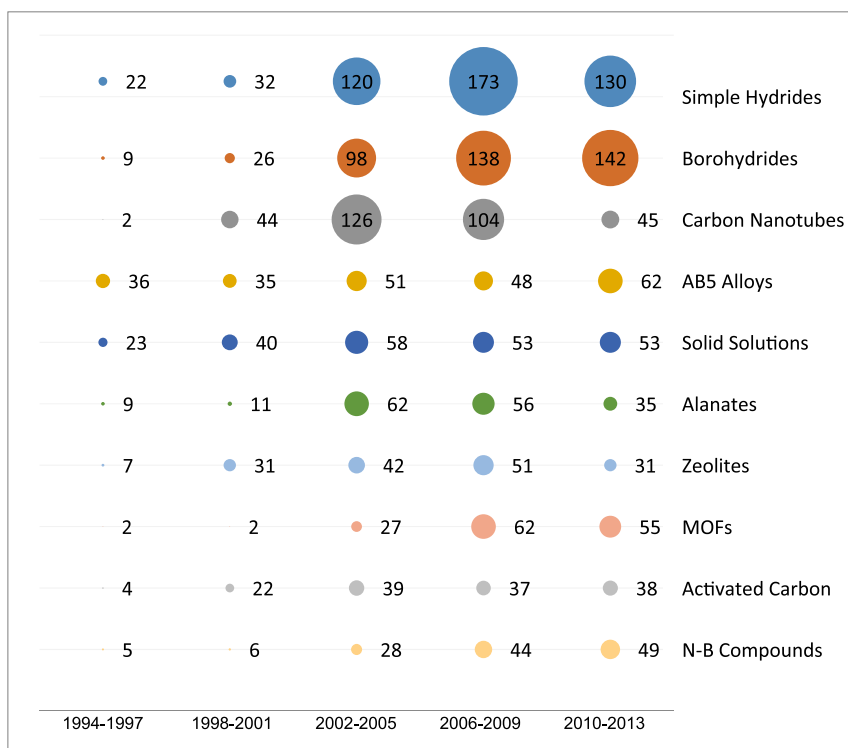


Fig. 11 – Time evolution of patent applications per HSM classes.

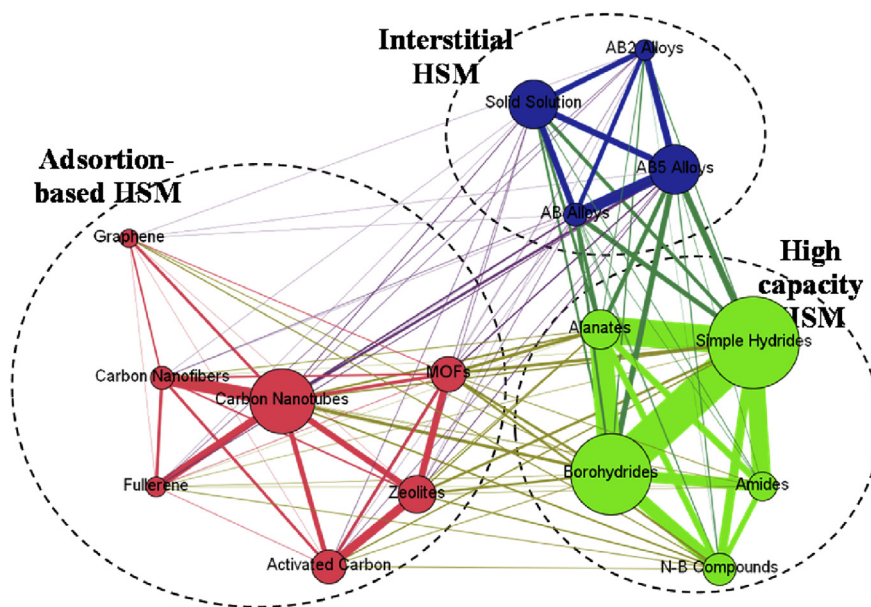


Fig. 12 – Network of co-occurrence of patenting among HSM classes. N.B.: The area of the circles represents the number of patents mentioning the class, and the thickness of the connections represents the number of patents mentioning both the connected classes.

technological progress. This seems to be the case, since scientific research on the theme is increasing, and hydrogen vehicles and stationary materials-based hydrogen storage solutions are starting to enter the market in commercial scale.

Although some HSM classes, like Carbon Nanotubes, show signs of abandonment, there is not yet a dominant

technology, so the array of technological alternatives to the problem is still open. There was, however, a higher patenting in the High Capacity HSM cluster, particularly for Simple Hydrides and Borohydrides.

While China has increased its patenting dramatically in recent years, opposing the general trend, it does not deposit its

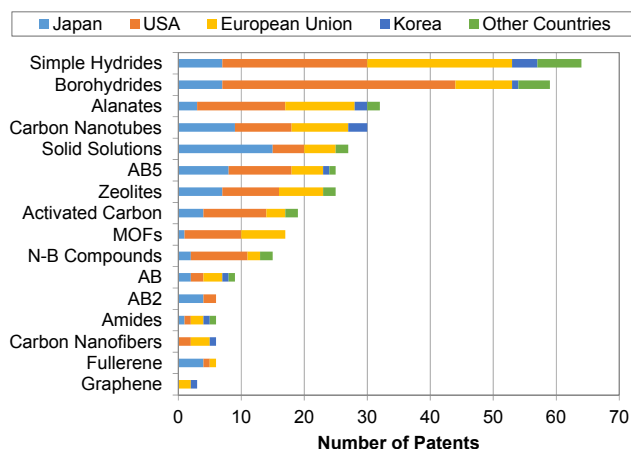


Fig. 13 – Triadic patents according to their geographical distribution and HSM class.

patents internationally, raising concerns about their economic value. Considering triadic patents, the most prominent territories are the USA and EU for Simple Hydrides, the USA for Borohydrides and Japan for Solid Solution Alloys. This could be indicative of future key players for these technologies.

There is still some uncertainty over HSM technological development, concerning both the technological life cycle stage and the selection of HSM classes. Continued monitoring is therefore necessary in the coming years for a better comprehension of the technological evolution of the field.

Funding

This work was supported by FAPESP [grant number 2015/18878-8] and CAPES PROEX.

Acknowledgements

The authors would like to thank CAPES and FAPESP (2015/18878-8) for the financial support; PPGCEM and NIT-Materiais UFSCar for the Infrastructure, Prof. Dr. Ariadne Chloe Furnival from the DCI-UFSCar for the English language revision, and the peer reviewers for their very meaningful contributions.

REFERENCES

- [1] Dunn S. Hydrogen futures: toward a sustainable energy system. *Int J Hydrogen Energy* 2002;27:235–64.
- [2] Schlapbach L, Züttel A. Hydrogen-storage materials for mobile applications. *Nature* 2001;414:353–8. <http://dx.doi.org/10.1038/35104634>.
- [3] Chanchetti LF. *Cientometria aplicada a materiais para armazenamento de hidrogênio*. Universidade Federal de São Carlos; 2014.
- [4] Sandrock G. Panoramic overview of hydrogen storage alloys from a gas reaction point of view. *J Alloys Compd* 1999;293:877–88. [http://dx.doi.org/10.1016/S0925-8388\(99\)00384-9](http://dx.doi.org/10.1016/S0925-8388(99)00384-9).
- [5] Chen P, Zhu M. Recent progress in hydrogen storage. *Mater Today* 2008;11:36–43.
- [6] Jain IP, Jain P, Jain A. Novel hydrogen storage materials: a review of lightweight complex hydrides. *J Alloys Compd* 2010;503:303–39. <http://dx.doi.org/10.1016/j.jallcom.2010.04.250>.
- [7] Staubitz A, Robertson APM, Manners I. Ammonia-borane and related compounds as dihydrogen sources. *Chem Rev* 2010;110:4079–124. <http://dx.doi.org/10.1021/cr100088b>.
- [8] Ströbel R, Garche J, Moseley PT, Jörissen L, Wolf G. Hydrogen storage by carbon materials. *J Power Sources* 2006;159:781–801. <http://dx.doi.org/10.1016/j.jpowsour.2006.03.047>.
- [9] Murray LJ, Dinca M, Long JR. Hydrogen storage in metal-organic frameworks. *Chem Soc Rev* 2009;38:1294. <http://dx.doi.org/10.1039/b802256a>.
- [10] Dong J, Wang X, Xu H, Zhao Q, Li J. Hydrogen storage in several microporous zeolites. *Int J Hydrogen Energy* 2007;32:4998–5004. <http://dx.doi.org/10.1016/j.ijhydene.2007.08.009>.
- [11] Sakintuna B, Lamari-Darkrim F, Hirscher M. Metal hydride materials for solid hydrogen storage: a review. *Int J Hydrogen Energy* 2007;32:1121–40. <http://dx.doi.org/10.1016/j.ijhydene.2006.11.022>.
- [12] Karkamkar A, Aardahl C, Autrey T. Recent developments on hydrogen release from ammonia borane. *Mater Matters* 2007;2:6–9.
- [13] Hirscher M. *Handbook of hydrogen storage: new materials for future energy storage*. Weinheim: WILEY-VCH; 2010.
- [14] Varin RA, Czujko T, Wronski ZS. *Nanomaterials for solid state hydrogen storage*. New York; London: Springer; 2008. <http://dx.doi.org/10.1007/978-0-387-77712-2>.
- [15] Huot J. Metal hydrides. In: Hirscher M, editor. *Handb. hydrog. storage new mater. futur. hydrog. storage*. Weinheim: WILEY-VCH; 2010. p. 368.
- [16] Moed HF, Glänzel W, Schmoch U. *Handbook of quantitative science and technology research: the use of publication and patent statistics in studies of S&T systems*. Dordrecht: Kluwer Acad. Publ; 2004.
- [17] Moge ME. Patents and technology intelligence. In: Ashton WB, Klavans TA, editors. *Keep abreast sci. technol. tech. intell. bus.* Columbus: Battelle Press; 1997. p. 295–335.
- [18] Milanez DH, Amaral RM do, Faria LIL de, Gregolin JAR. Technological indicators of nanocellulose advances obtained from data and text mining applied to patent documents. *Mater Res* 2014;17:1513–22. <http://dx.doi.org/10.1590/1516-1439.266314>.
- [19] Milanez DH, Amaral RM do, Faria LIL de, Gregolin JAR. Assessing nanocellulose developments using science and technology indicators. *Mater Res* 2013;16:635–41. <http://dx.doi.org/10.1590/S1516-14392013005000033>.
- [20] Porter AL, Detampel MJ. Technology opportunities analysis 1995;49:237–255.
- [21] Ernst H. The use of patent data for technological forecasting: the diffusion of CNC-technology in the machine tool industry. *Small Bus Econ* 1997;9:361–81.
- [22] OECD. *OECD patent statistics manual*. Paris: Organisation for Economic Co-operation and Development; 2009.
- [23] nsf.gov – Science and Engineering Indicators 2012-US National Science Foundation (NSF) n.d. <https://www.nsf.gov/statistics/seind12/start.htm> [accessed 19.07.16].
- [24] Bakker S, Budde B. Technological hype and disappointment: lessons from the hydrogen and fuel cell case. *Technol Anal Strateg Manag* 2012;24:549–63. <http://dx.doi.org/10.1080/09537325.2012.693662>.
- [25] Fenn J, Raskino M. *Mastering the hype cycle: how to choose the right innovation at the right time*. Harvard Business Press; 2008.

- [26] Steinert M, Leifer L. Scrutinizing Gartner's hype cycle approach. 2010. p. 254–66.
- [27] Gisler M, Sornette D, Woodard R. Innovation as a social bubble: the example of the human genome project. *Res Policy* 2011;40:1412–25. <http://dx.doi.org/10.1016/j.respol.2011.05.019>.
- [28] Bakker S. Hydrogen patent portfolios in the automotive industry—the search for promising storage methods. *Int J Hydrogen Energy* 2010;35:6784–93. <http://dx.doi.org/10.1016/j.ijhydene.2010.04.002>.
- [29] Shih H-YH, Yen S-YS. A patent analysis of hydrogen storage techniques in Taiwan: a preliminary study of the overall industry. In: *Technol. manag. energy smart world (PICMET), 2011 proc. PICMET'11. IEEE; 2011*. p. 1–7.
- [30] Chen YH, Chen CY, Lee SC. Technology forecasting and patent strategy of hydrogen energy and fuel cell technologies. *Int J Hydrogen Energy* 2011;36:6957–69. <http://dx.doi.org/10.1016/j.ijhydene.2011.03.063>.
- [31] International Patent Classification (IPC) n.d. <http://www.wipo.int/classifications/ipc/en/> [accessed 19.07.16].
- [32] Derwent Innovations Index | Thomson Reuters n.d. <http://thomsonreuters.com/en/products-services/scholarly-scientific-research/scholarly-search-and-discovery/derwent-innovations-index.html> [accessed 19.07.16].
- [33] Search Technology I. VantagePoint n.d. <https://www.thevantagepoint.com/> [accessed 19.07.16].
- [34] Bastian M, Heymann S, Jacomy M. Gephi: an open source software for exploring and manipulating networks. In: *Third int. AAAI conf. weblogs soc. media; 2009*. p. 361–2. <http://dx.doi.org/10.1136/qshc.2004.010033>.
- [35] Blondel VD, Guillaume J-L, Lambiotte R, Lefebvre E. Fast unfolding of communities in large networks. *J Stat Mech Theory Exp* 2008;2008:P10008. <http://dx.doi.org/10.1088/1742-5468/2008/10/P10008>.
- [36] Campbell RS. Patent trends as a technological forecasting tool. *World Pat Inf* 1983;5:137–43. [http://dx.doi.org/10.1016/0172-2190\(83\)90134-5](http://dx.doi.org/10.1016/0172-2190(83)90134-5).
- [37] IEA – Japan n.d. <http://www.iea.org/policiesandmeasures/pams/japan/name-21045-en.php> [accessed 19.07.16].
- [38] The White House. Fact Sheet: Hydrogen Fuel: a Clean and Secure Energy Future 2003. <http://georgewbush-whitehouse.archives.gov/news/releases/2003/02/20030206-2.html> [accessed 19.07.16].
- [39] FreedomCAR and Fuel Partnership Plan n.d. https://www.hydrogen.energy.gov/pdfs/fc_fuel_partnership_plan.pdf.
- [40] Kommission E. European fuel cell and hydrogen projects: 2002–2006. Luxembourg: Office for Official Publications of the European Communities; 2006.
- [41] Dang J, Motohashi K. Patent statistics: a good indicator for innovation in China? Patent subsidy program impacts on patent quality. *China Econ Rev* 2013;35:137–55. <http://dx.doi.org/10.1016/j.chieco.2015.03.012>.
- [42] Fisch CO, Block JH, Sandner PG. Chinese university patents: quantity, quality, and the role of subsidy programs. *J Technol Transf* 2016;41:60–84. <http://dx.doi.org/10.1007/s10961-014-9383-6>.
- [43] DOE Hydrogen and Fuel Cells Program: Budget n.d. <https://www.hydrogen.energy.gov/budget.html> [accessed 19.07.16].
- [44] Bakker S. The car industry and the blow-out of the hydrogen hype. *Energy Policy* 2010;38:6540–4. <http://dx.doi.org/10.1016/j.enpol.2010.07.019>.
- [45] Q & A: Steven Chu | MIT Technology Review n.d. <http://www.technologyreview.com/news/413475/q-a-steven-chu/> [accessed 19.07.16].
- [46] Stephen Chu changes his mind on fuel cells – Fracking and oxyfuel – The Hydrogen Journal n.d. <http://www.thehydrogenjournal.com/displaynews.php?NewsID=688&PHPSESSID=gg24ikbknb618jah11b97qn7> [accessed 19.07.16].
- [47] Toyota Global Site | Fuel Cell Vehicle. Toyota Glob Site n.d. http://www.toyota-global.com/innovation/environmental_technology/fuelcell_vehicle/ [accessed 19.07.16].
- [48] McPhy – Milestones n.d. <http://www.mcphy.com/en/about/milestones/> [accessed 19.07.16].
- [49] Hydrexia Australia n.d. <http://hydrexia.com/> [accessed 19.07.16].
- [50] EPO – Patent families n.d. <https://www.epo.org/searching-for-patents/helpful-resources/first-time-here/patent-families.html> [accessed 19.07.16].