

Current research trends and prospects among the various materials and designs used in lithium-based batteries

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Abstract Increasing energy consumption, shortages of fossil fuels, and concerns about the environmental impact of energy use, especially emissions of carbon dioxide, give fresh impetus to the development of renewable energy sources. With the advent of renewable energy, it is now indispensable that efficient energy storage systems have to be developed. One of the most promising storage systems to be employed in stationary energy storage applications are lithium-based batteries (LIB), mainly due to their high energy density, high power, and nearly 100 % efficiency. Within the scope of this paper, we carry out a patent search using the patent database PatBase[®] to assess the development status of LIB technology. The analysis of the generated patent sample reveals disproportionately high growth rates in LIB patent applications over the last years compared to other selected energy-related technologies. Breaking down patent application growth by the different components of LIB shows the principal drivers of growth.

The purpose of this paper is to provide current research trends and prospects for the main LIB materials and designs.

Keywords Lithium-based batteries · Patent-analysis · Technology status · Research trends · Forecasting

1 Introduction

One of the greatest challenges in the 21st century is to stabilize a consistent and sustainable energy supply that will meet the world's increasing energy demands. Thus, it is crucial to improve energy efficiency and to expand renewable energy—not only because of the current global context of rising energy demand and energy prices but also because of the challenge to reduce the emission of greenhouse gases, especially those of carbon dioxide, to prevent global warming [1].

Following the Fukushima nuclear power plant disaster, the German government has reevaluated the residual risks of nuclear power and decided to phase-out the use of nuclear power until the end of 2022. Based on their new Energy Concept, the German government aims to cover at least 35 percent of the German electricity consumption with renewable energy by 2020 at the latest [1, 2].

However, many renewable energy sources, such as solar photovoltaic and wind are unavailable during extended periods of time. The generated power from these sources is always fluctuating due to the environmental status. Hence, with the advent of renewable energy, a new demand for energy storage systems emerges [3]. Particularly, energy storage systems based on lithium-based batteries (LIB) are being widely regarded as one of the near-term solution to deal with the variations of renewable energy sources [4, 5].

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LIB have gained a lot of attention since their commercialization in 1991 because of their superior energy density and cycle life compared to other battery systems [6–8]. Figure 1 outlines the specific power versus the specific energy of LIB contrasted to other common battery systems.

These benefits, along with fast discharge capabilities, have made LIB almost ideal for usage in portable electronics. However, to be implemented in large-scale high power systems such as plug-in hybrid electric vehicles, plug-in electric vehicles or stationary energy storage systems at grid-scale, cost targets as well as performance requirements are raised especially from the aspects of energy density, cycling life, and safety issues, therefore further advances in LIB materials and devices are essential.

The speed and scope of research and development of LIB make it critical for researchers to be aware of the progress in this field across different laboratories. Thus, in a first step, the current paper aims at giving a general overview on the research activities in the field of LIB. To this end, we conduct a patent search on LIB and their main components. We identify the main fields of patent activity in LIB and give an overview on the state-of-the-art in LIB technology. In a second step and based on our first findings, we aim at forecasting possible future research trends among the various battery components, main materials, and dominant designs used in LIB.

The remainder of this paper is structured as follows. In the next section, we will briefly introduce the functional principle of LIB and discuss the use of patent data to describe the status of technology systems and the applicability of patent data as sources for technological forecasting. Afterward, the applied research design will be explained in detail and we will present and discuss our major results in Sect. 4. Finally, we will draw conclusions and provide an outlook on possible future research.

2 Theory

2.1 Brief introduction to the functional principle of LIB

Basically, LIB consist of a negative electrode, a positive electrode, and a separator, which is soaked with electrolyte, to ensure the charge transfer within the battery. The separator itself, as an electrical insulator, prevents a short circuit between both electrodes and at the same time allows rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current within the cell. The electrode materials are coated on current collectors, whereas copper is used for the negative electrode and aluminum for the positive electrode (cf. Fig. 2).

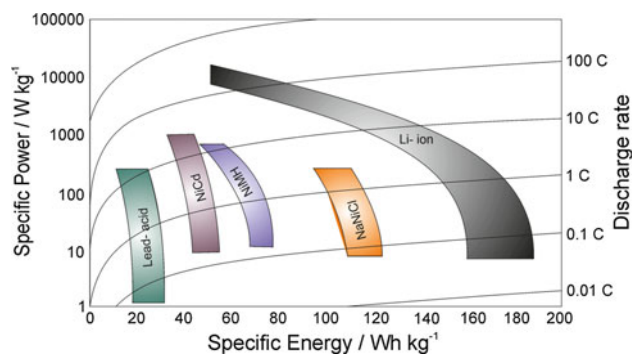


Fig. 1 Specific power versus specific energy plot of different battery types. Source own figure based on [73]

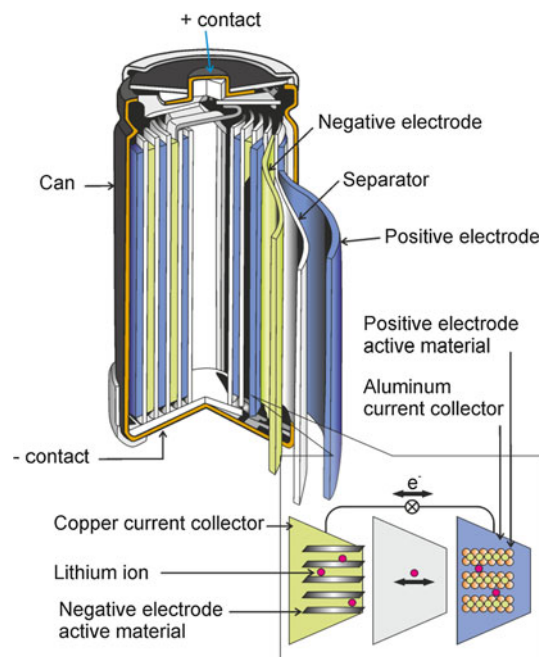


Fig. 2 Schematic depiction of a lithium-ion battery

During the charge process, reduction occurs at the negative electrode (anode). In this process, the anode withdraws electrons from the positive electrode (cathode) through the outer circuit and simultaneously inserts lithium ions, deriving from the electrolyte and the cathode material, to ensure the charge balance. As a result, the cathode material is oxidized. In the case of the discharge process, the redox reactions are inverted. The electrochemical roles of the electrodes change between anode and cathode, depending on the direction of the current flow through the cell. Different materials are used both for the electrodes and the separator as well as for the electrolyte. The main trends and developments in these fields are revealed by the patent analyses in Sect. 4 of this paper.¹

¹ For further information on LIB see: [9].

2.2 Patents as indicators for technological analyses

Before explaining why patents are widely used as technology indicators, we will introduce patents in general. To begin with, a patent has two important functions: First, a patent allows its holder to exclude others from exploiting the invention covered by the patent in a certain country and for a specific period. Second, a patent stimulates invention and promotes the disclosure of inventions, which in turn should foster economic progress [10].

A patent application is generally filed at a national patent office. This initial filing is considered as the priority filing from which further successive national, regional, or international filings can be made within the priority period of 1 year. The date of the initial application is the *priority date*. If there are further applications for an individual invention (e.g., in other countries), claiming the same priority, these single patent documents form a *patent family*.² In most countries, patent application are disclosed 18 months after the priority application, regardless of whether it has yet been granted or not. If the patent is granted the protection period, which guarantees an exclusive exploitation right for up to 20 years, starts at the priority date.

Patents are a significant source of technical information, as they are often the first source of published information on new technologies. If technical information is first disclosed in a patent, there is only a small chance that it is disclosed later again in non-patent literature. It is supposed that 80 % of the information disclosed in patents is not published elsewhere [11]. Thus, the analysis of bibliometric data, derived from patents, is considered to be one of the most efficient methods to illustrate and quantify research activities and technology output within a certain technology field [10].

In detail, patents offer a worldwide geographical coverage as well as coverage of nearly every technology field. In addition, patent data are readily available and largely free of errors as they are the result of legal examinations. Since there is a statistically significant relationship between patent counts and the output of industrial research and development (R&D) and other innovative activities, patent data are currently regarded as the best indicators for measuring and mapping scientific and technological activity. Nevertheless, we are facing some limitations when using patent data as measure of technological progress. First, information disclosed in patents differs in their technological and economic importance. The minority of patents relates to inventions of high technological or economic value, whereas the bulk of patents are of only marginal

value. Second, the propensity to patent varies across firms, technology fields, and countries. Third, the patent application process is not homogeneous. There is substantial variation among the various national patent systems, in terms of legal, economic, and cultural factors [10].

2.3 The use of patent data for technological forecasting

It is widely accepted in literature that technological performance over lifetime (or cumulative R&D expenditures) follows a S-shaped relationship [12, 13]. The S-curve consists of at least four different areas: starting with a slow initial rising in the emerging stage, an accelerated increasing follows in the growth stage before it ends up in a diminishing rising in the maturity stage, and finally a stagnation in the saturation stage (cf. Fig. 3).

A major challenge of the S-curve concept is the selection of an appropriate performance measure. As explained in the previous section, patenting activity reflects the latest state-of-the-art in technological development. It is therefore an appropriate measure for technological performance. Furthermore, patent data integrate an economic point of view into the S-curve concept, as there is a positive relationship between patenting activity and market changes [14, 15].

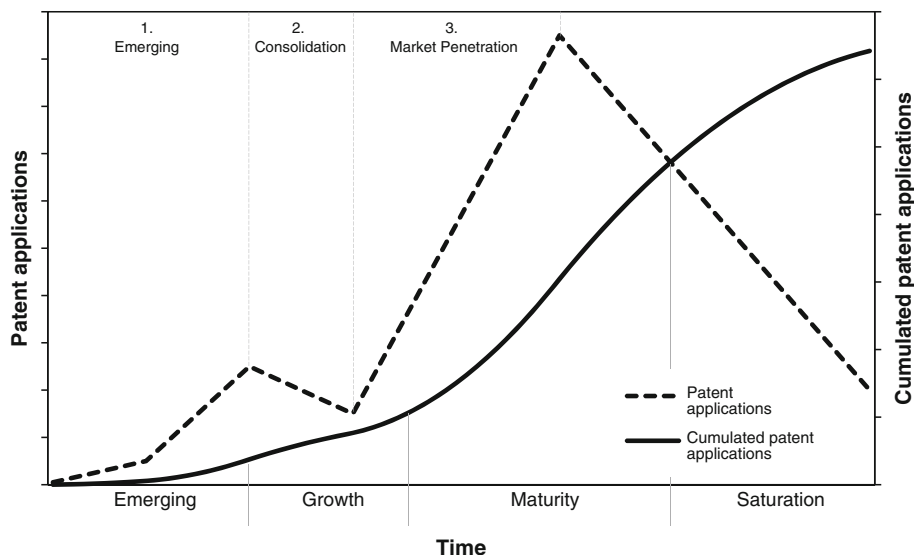
It is well shown [12] that patent data obviously can mirror different technological development stages. Figure 3 illustrates the theoretical development of patenting activity, as measured by patent applications, over time. Basically, three different development stages (emerging, consolidation, and market penetration) can be distinguished to evaluate technologies according to their development status. Consequently, the analysis of patent data in a technological area is regarded as a suitable and valuable forecasting tool [12].

3 Research design

We used the patent database PatBase[®] from Minesoft and RWS Group to conduct our analyses. PatBase[®] provides access to patent documents from over 95 issuing authorities worldwide and contains more than 45 million patent families. In PatBase[®], patents are grouped into families if they contain one or more common priorities with other patents. This type of family grouping is often referred to as extended families and is used by the European Patent Office (EPO). The advantage of extended families is that the results are already de-duplicated and pre-grouped, which saves time by avoiding duplication. Furthermore, PatBase[®] includes integrated software tools to instantly analyze and export relevant patent data.

² For details see: <http://www.epo.org/searching/essentials/patent-families.html>, accessed November 2012.

Fig. 3 The theoretical development of patenting activity over the technological life cycle referring to *Ernst* [12]



Keyword-based searches are probably the most commonly used approach to create a patent sample representing a specific technological field. However, in essence, keywords are subjective. In consequence, the exclusive use of keywords in a patent search cannot be a reliable basis to attain a comprehensive and full result.

Before their publication, patent documents are given one or more classification codes based on their textual contents for topic-based analysis and retrieval. All patents are individually classified using a standardized system, the International Patent Classification (IPC) system. In contrast to the use of keywords as search terms for patent analyses, the use of the IPC-classification codes are more objective. However, the classification system is limited in its depth of detail and degree of differentiation. Most of the time, the pre-defined categories do not meet the goal for a particular analysis [16].

For this reason, we use a combination of IPC classification codes and rather precise keywords, including the use of Boolean and proximity operators as well as truncation, for our patent search. In order to attain a complete set of relevant patents, the keyword search was carried out using the full text of the patent documents. Taking the patent documents from the United States Patent and Trademark Office (USPTO) as examples, full text search includes: title, abstract, claims, and description of the invention, whereas the latter can be further divided into field of the invention, background, summary, and detailed description. Although some patents may not consist of all these segments, most patents do follow this specific structure [17]. All reported results in this paper are based on full search, except where it is specified otherwise. Table 1 lists the complete applied research algorithm. For the statistical analyses, we used VizPat, an integrated software tool in PatBase®.

4 Results and discussion

First, we present a historical trend, based on the patent publication dates, for LIB in general over the period from 1990 to 2010. Following this, we show the major results of our patent search regarding the patent application trends among the different battery components, main materials, and dominant designs used in LIB. Moreover, we try to identify the core areas and prospects of research for selected components within the field of LIB.

4.1 Historical trend

In Fig. 4, the historical trend of patenting activity in the field of LIB is depicted, as measured by the annual number of patent family applications and the cumulated number of patent family applications, over time.³ Starting in the early 1980s, the LIB was developed in Japan by *Asahi Kasei Co.* and first commercialized by *Sony Co.* in 1991. It was only then that the battery community worldwide accepted the LIB technology. Before 1990, the patenting activity is relatively low. This is why we focus our patent search on the period between 1990 and 2010. Analyzing Fig. 4, the pattern of patenting activity in the field of LIB basically follows the previously discussed theoretical technology development model based on patent applications, which is shown in Fig. 3. The period from its introduction in 1991–2000 was a time for establishing the fundamental base for materials and manufacturing processing. The first increase in the number of patent families between 1995 and 2000 signaled the end of the fundamental technological

³ These patent family applications are subsequently termed as patent families, whereby each patent family consists of at least one patent application without regard to the status of being granted later on.

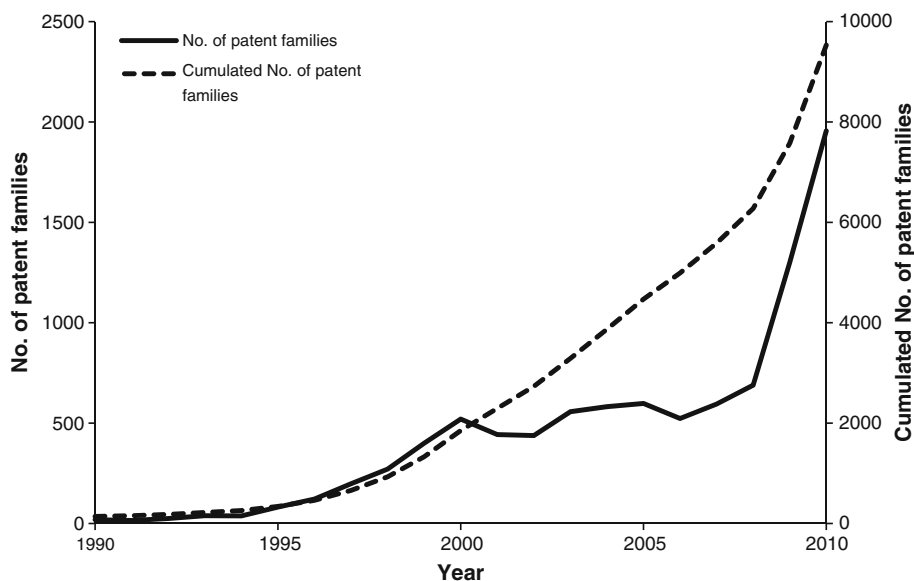
Table 1 Applied research algorithm

Nr.	Field of research	Algorithm
1	Lithium accumulator	ipc = h01m10/052*
	Electrodes	1 and IPC = (H01M4/13* or H01M4/36 or H01M4/38 or H01M4/46 or H01M4/48* or H01M4/50* or H01M4/52* or H01M4/58*)
	Current collector	1 and IPC = (H01M4/64 or H01M4/66 or H01M4/70)
	Separator	1 and IPC = (H01M2/14 or H01M2/16 or H01M2/18)
	Electrolyte	1 and IPC = (H01M10/056*)
	Inactive substances as ingredients for active masses	1 and IPC = (H01M4/62)
2	Cell housing	1 and IPC = (H01M2/02 or H01M2/04 or H01M2/06 or H01M2/08)
	LCO	1 and FT = (lithium cobalt oxide or LiCoO ² or Li ^x CoO ² or LCO)
	Spinel	1 and FT = (lithium manganese oxide or lithium nickel manganese oxide or LiMn ² O ⁴ or LMO or LiNi ^{0.5} Mn ^{1.5} O ⁴)
	NCM	1 and FT = (lithium nickel manganese cobalt oxide or NCM or NMC or LiNiMnCoO ² or (((Li w3 Ni) w3 Mn) w3 Co) O ²) or LiNi ^{1/3} Mn ^{1/3} Co ^{1/3} O ²)
	Olivine	1 and FT = (lithium iron phosphate or LiFePO ⁴ or LFP or olivine# or LiMPO ⁴ or LiNiPO ⁴ or LiMnPO ⁴ or LiCoPO ⁴)
	NCA	1 and FT = (lithium nickel cobalt aluminum oxide or NCA or LiNiCoAlO ² or LiNi ^{0.80} Co ^{0.15} Al ^{0.05} O ²)
	Graphite	1 and IPC = H01M4* and FT = (graphite or graphitic carbon#)
	Hard carbon	1 and IPC = H01M4* and FT = (hard carbon# or non-graphitizing carbon#)
	Soft carbon	1 and IPC = H01M4* and FT = (soft carbon# or (graphitizing carbon# not (non-graphitizing)))
	Silicon based	1 and IPC = H01M4* and FT = (silicon# or Si) or IPC = C01B33*
	Tin based	1 and IPC = H01M4* and FT = (tin or Sn) or IPC = C01G19
	Titanium based	1 and IPC = H01M4* and FT = (titanium or Ti or Li ⁴ Ti ⁵ O ¹² or LTO or lithium titanate) or IPC = C01G23*
	Lithium metal	1 and IPC = H01M4* and FT = ((metallic lithium not (non-metallic)) or lithium metal or lithium anode or lithium electrode)
	Solid electrolyte	1 and IPC = H01M10/0562
	Polymer electrolyte	1 and IPC = H01M10/0565
	Ionic liquid	1 and IPC = H01M10/056* and (ionic liquid# or room temperature molten salts)
	Additives	1 and IPC = H01M10/0567
	Salt	1 and IPC = H01M10/0568
	Solvent	1 and IPC = H01M10/0569
	Cylindrical cell	2 and FT = (cylindrical# or 18650)
Prismatic cell	2 and FT = (prismatic# or hard case#)	
Pouch	2 and FT = (pouch# or coffee bag#)	

development phase and the upcoming of the new technology in portable electronic devices. The growth in patent activity during this time is mainly driven by rising performance requirements due to the proliferation of portable electronic devices. In the second phase, between 2001 and

2006 the annual growth in the number of patent families is lower, even slightly negative, compared to the preceding phase. Over this period, the cell production in China and Korea began to ramp up [18]. In order to reap profits in such an industry, a firm must produce at a high volume to

Fig. 4 Historical trend of patent activity in the field of LIB, as measured by the annual number of patent families and the cumulated number of patent families, over the time (1990–2010). Source PatBase®, July 2012



overcome thin margins. Thus, R&D efforts are often cut back. Beginning in 2003, the drive to increase capacity and performance for the competitive notebook and cellular phone applications continues [18]. This requires the development and introduction of higher performance electrode materials. The sharp rising in the annual number of patent families since 2009 indicates the third phase, the emerging market opportunities of LIB in large-scale high power systems.

Looking at the development of the cumulative patent families, the S-curve concept can be applied. Accordingly, it can be seen that the technology has just entered the maturity stage, in which the marginal growth of technological improvements, as indicated by patenting activity, follows a concave shape. The average annual growth rate in the number of patent families for 2006–2010 amounts to 32 %. Whereas the average annual growth rate in the same period for the IPC-Class H01M, covering primary as well as secondary batteries and fuel cells amounts to only 6 %.⁴ This comparison indicates disproportionately high growth rates in LIB patent activity. Since differences in patent activity across technology fields reflect their size, level of development, and technological impact one might forecast that LIB technology will play a key role within the energy storage sector during the next years. Referring to the S-shaped technological development pattern, the entrance of LIB technology into a saturation stage should lay in the distant future, considering the high growth rates and the possible future implementation of LIB in the transportation sector as well as in large-scale stationary storage systems.

⁴ Source: PatBase®, July 2012.

4.2 Components of LIB

Figure 5 illustrates the trend of patenting activity among the major components used in LIB, as measured by the total number of patent families and the average annual growth rate in the number of patent families for the period between 2006 and 2010. The electrodes and the electrolyte account for the largest numbers of patent families. They are the key research areas, not least because their improvement is essential for overall battery performance enhancement. Regarding the average annual growth rates for the period between 2006 and 2010, a shift in the main research areas begin to occur. Cell housing records the highest growth rate (38 %). This sector has grown at a faster rate than the overall LIB technology (32 %) has. Patent activity on the current collector, the electrolyte and the inactive substances as ingredients for active masses, e.g., binders and fillers, have increased at similar rates as the overall LIB technology, whereas that on the electrodes as well as on the separator show lower growth rates. In the following sections, the main materials and dominant designs, which are the principal drivers of growth among the battery components, are identified.

4.3 Positive electrode materials (cathode materials)

The commonly used LIB that power almost all portable electronics today are comprised of a graphite anode and a lithium cobalt oxide (LiCoO₂, LCO) cathode. This system generates a cell voltage of around 3.7 V and can reach a practical energy density of 150 Wh kg⁻¹ in single cells [9, 19]. Since the product of the operating voltage and the practical specific charge determines the energy of a battery,

Fig. 5 Patent application trend regarding the major components of a LIB, as measured by the total number of patent families and the average annual growth rate in the number of patent families for the period between 2006 and 2010. *Source* PatBase®, July 2012

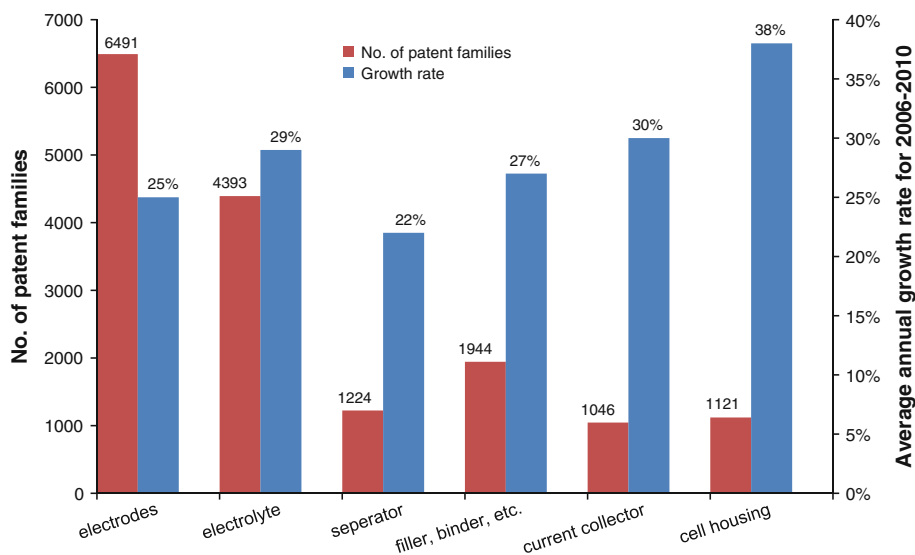
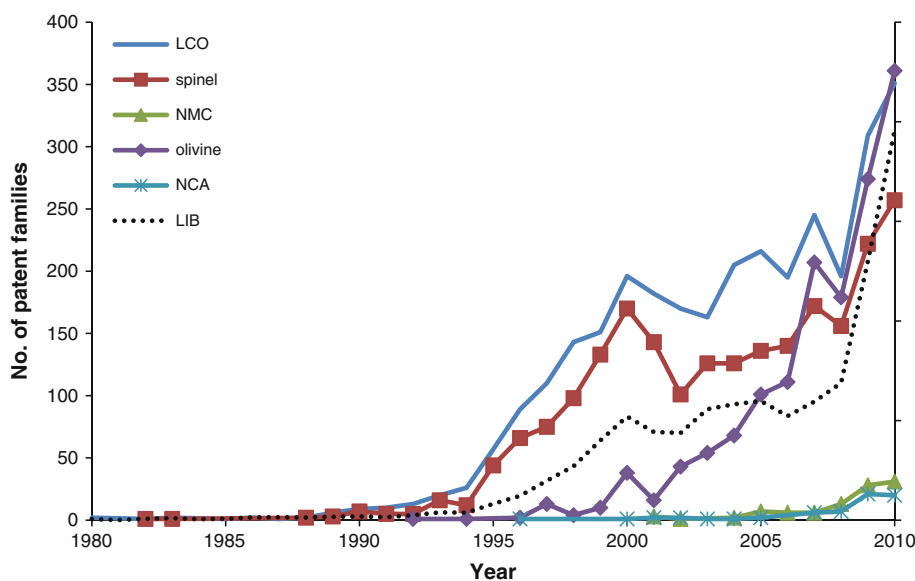


Fig. 6 Historical trend of patent activity for the various positive electrode materials, as measured by the annual number of patent families. *Source* PatBase®, July 2012



electrode materials must meet two fundamental requirements to reach the goal of a high specific energy (expressed in Wh kg^{-1}) system. First, a high specific charge (in mAh g^{-1}), and, second, a high (positive electrode) and a low (negative electrode) standard redox potential of the respective electrode redox reaction are ideal. Within LIB research, the negative electrode material (mostly graphite) is well optimized with regard to the theoretical specific energy and only minor improvements can be gained in terms of design changes. Therefore, the current goal of the battery community is to develop new positive electrode materials, which provide higher potentials and larger specific charges, to increase the resulting energy of the battery [20]. Besides the specific energy, the following designing criterions are often considered: rate capability, cycling performance, safety, and costs.

In Fig. 6, the historical trend of patenting activity for the most commonly used positive electrode materials is shown. For this study, we combine the IPC codes H01M10/52 and H01M10/525, which cover Li-accumulators as well as lithium-ion batteries, respectively, with multiple keywords, describing the individual cathode materials. For reasons of comparison, we include the historical trend of patenting activity in the general field of LIB in this figure. When interpreting the patent data, it should be kept in mind that our patent search is based on the full text of each patent document. Therefore, not all of these patents identified by our search relate to a new invention concerning the particular positive electrode material.

LiCoO_2 (LCO) was identified to act as positive electrode material of lithium batteries in 1980 by *Goodenough* and coworkers [21]. Since it provides a potential of around

3.9 V versus Li/Li^+ [22], it was successfully introduced as a cathode material of the newly invented LIB by *Sony* in 1991 and is still one of the most frequently used positive electrode materials. The importance of LiCoO_2 as active material is also reflected in the patent data. The largest number of patent documents has reference to LiCoO_2 . However, the rapid rise of its price due to the lack of cobalt resources as well as its relative low practical specific charge—it can only deliver about 140 mAh g^{-1} (cf. also Fig. 7), which is half of its theoretical specific charge—and disadvantages concerning aspects of stability and toxicity have promoted the development of alternative active materials [23, 24]. Looking at the development of the annual number of patent families, the curve for LiCoO_2 has a similar shape to that of overall LIB. Considering the tasks of LIB in the transportation sector as well as in large-scale stationary storage systems and the presence of toxic and expensive Co ions, LiCoO_2 is supposed to be in the late phase of the maturity stage, where the potential of further technological progress seems to be restricted. With the exception of the years 2009 and 2010, in which overall patent activity in LIB dramatically increases, the rate of growth in patent applications has already start to slow down and new competitive active materials begin to dominate the market.

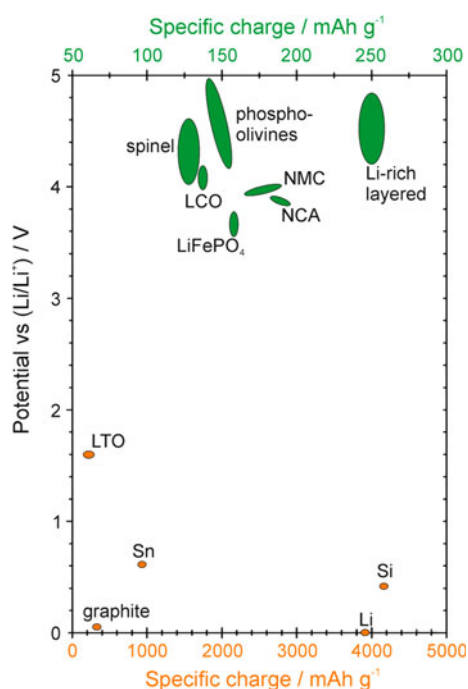


Fig. 7 Schematic plot of the potential versus the specific charge of various positive and negative electrode materials. *Note* Alloy negative electrode materials are represented in the maximum lithiated phase ($\text{Li}_{4.4}\text{Si}$ and $\text{Li}_{4.4}\text{Sn}$). The specific charges of the negative electrode materials are based on the un lithiated forms. Therefore, a fair comparison between the Li-storage materials and pure Li metal is not possible

Among them, LiNiO_2 has been a target compound since the initial stage of the research, because it is isostructural with LiCoO_2 (layered oxides), is lower in costs and provides a higher energy density as compared to LiCoO_2 . In spite of extensive research, LiNiO_2 is not commercialized in the pure state yet. This is mainly due to difficulties in preparation and safety concerns. Thermal stability of LiNiO_2 at charged state is so low that the cell suffers from thermal runaway. There is much effort to overcome the safety problem by partial substitution of nickel with other elements. Particularly, aluminum is used as a co-dopant with cobalt in LiNiO_2 . The best known derivative is $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ (NCA), which is used in a small scale for commercial application [25]. Its development was put forward by the Department of Energy's Advanced Technology Development program based at *Argonne National Laboratories* in 2000s [26]. Therefore, a slight increase in patent activity could be expected during this period. The strengths of the NCA-system include high energy and high power due to its relatively high specific charge of about 180 mAh g^{-1} and an average voltage of about 3.9 V [27]. Although NCA is already used in commercial applications, work remains to be done in terms of safety, costs, and the useful fraction of the state of charge range.

A crucial problem of these high Ni content materials, like NCA, is the rapid reaction with air resulting in the formation of Li_2CO_3 and LiOH on the surface, leading to a reduction in capacity and increased irreversible capacity of the active material [28, 29].

Our patent analysis confirms that NCA is a relative new positive electrode material, still being in the beginning of the emerging stage, in which the future development is uncertain. Since NCA is one of the most proven cathode materials, the potential of further technological progress seems to be limited, first and foremost in regard to cost issues.

Further layered oxides to be mentioned here are the so-called NMC type materials, based on the three transition metal ions of nickel, manganese, and cobalt. The most commonly used NMC composition contains equal amounts of these three transition metals. $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ was firstly reported as positive electrode material in 2001 by *Ohzuku* and *Makimura* and is already successfully commercialized [30]. NMC cathodes deliver specific charges around 160 mAh g^{-1} (with an anodic cut-off potential of 4.2–4.3 V) and an average voltage of about 3.9 V [27]. However, cycle life, specific charge, and safety depend on the upper cut-off potential. The challenges remaining for these materials include stabilization during prolonged cycling and improving their rate capabilities as well as safety features [19]. But, their overall performance is at least equal to or superior to LiCoO_2 electrodes [23]. The

patent data display that NMC is the newest positive electrode material in our study and has just entered the emerging stage of the technological life cycle. In comparison to NCA, its overall number of patent families is about 50 % higher and consequently its competitive impact is higher. The average annual growth rate in the number of patent families for 2006–2010 amounts to 46 %. Whereas LiCoO₂ has grown at a rate of 13 %. Consequently, NMC seems to be a promising positive electrode material. But, with due regard to cost targets, NMC could only be a short term solution.

A new class of cathode materials are the so-called Li-rich layered transition metal oxides of the (Li₂MnO₃)_x(LiMO₂)_{1-x} type. Since the patent data on this class of materials is sparse so far, we decided not to include them in our patent analyses. Li-rich layered transition metal oxides, being examined worldwide as a novel high energy cathode material, were developed by the end of the 1990s, *inter alia*, at the Argonne National Laboratories [31–34].

With excess Li ions introduced in the system, the specific charge of this series of materials can be increased to more than 250 mAh g⁻¹, but this high capacity is only available at moderate rates [35]. These compounds operate within a wide voltage range (cf. Fig. 7). The challenges remaining for these materials include stabilization during prolonged cycling due to continuous structural changes in the material, improving their rate capabilities and their large first cycle irreversible capacity as well as demonstrating acceptable safety features [19]. Li-rich layered transition metal oxides are a relative new technology. They are still in the beginning of the emerging stage, in which the future development is uncertain.

Compromises on cell performance can only be made if there are intrinsic cost advantages. This is the reason why naturally abundant, low cost, and environmentally friendly LiMn₂O₄ (spinel), despite having an accessible specific charge 5–10 % smaller than LiCoO₂ and suffering from capacity fading problems, was the first to be considered as a possible alternative cathode material [36]. Thackeray and coworkers originally proposed LiMn₂O₄ as a positive electrode material already in 1983 [37]. But, it was not before 1996 that LiB based on spinel-type LiMn₂O₄ cathodes were commercialized [25]. The spinel, that is mainly used, is one in a stabilized form in which a part of the manganese ions has been substituted with other metal ions. The most common addition to LiMn₂O₄ is nickel. Among these derivatives, LiNi_{0.5}Mn_{1.5}O₄—first reported in 1997—shows the best overall electrochemical performance [38]. Compared to LiMn₂O₄ spinel the voltage is lifted from 4.1 to 4.7 V and the specific charge amounts to 140 mAh g⁻¹, whereas LiMn₂O₄ only offers about 120 mAh g⁻¹. Despite the practical specific charge of this high voltage spinel is as low as the one of LiCoO₂ and the rate capability still needs

to be improved, LiNi_{0.5}Mn_{1.5}O₄ is a suitable positive electrode material for large-scale use in LIB [24]. The development of the number of the annual patent families indicates that the spinel seems to be in the maturity stage. The average annual growth rate in the number of patent families for 2006–2010 amounts to 15 % and is only slightly higher compared to that of LiCoO₂. Consequently, compared to LiCoO₂, the competitive impact of the spinel is even lower. In order to ensure a fair comparison between LiNi_{0.5}Mn_{1.5}O₄ and the other cathode materials, it is necessary to state, that the further technological progress of high voltage cathode materials is mainly dependent on the development of electrolytes stable against decomposition by oxidation. Electrolytes will be addressed in more detail in Sect. 4.5.

Since the pioneering work of Goodenough and coworkers in 1997 phospho-olivine compounds (LiMPO₄)—where M may be Fe, Mn, Co, or Ni, exhibiting the following redox potentials: 3.5, 4.1, 4.8, and 5.2 V versus Li/Li⁺, respectively—are characterized as promising cathode materials [19, 39–41]. However, among them, only LiFePO₄ has become one of the most important practical cathode materials. LiFePO₄ reaches a specific charge of approximately 165 mAh g⁻¹ and is low cost, non-toxic, and environmentally friendly. Although it demonstrates excellent cycling performance and safety features, the main drawbacks of this material lie on its low specific energy limited by the voltage, and its poor rate capability, caused by a low conductivity [24]. Nevertheless, the development of the annual patent families shows that phospho-olivine compounds are currently the materials with the highest competitive impact. These compounds have the third largest number of matching patent documents and have an average annual growth rate in the number of patent families for 2006–2010 of 34 %. With regard to the technological life cycle concept, phospho-olivines are found to be in the maturity stage. Their good characteristics make them a suitable choice for large-scale applications.

4.4 Negative electrode materials (anode materials)

Before the launch of the commercial LIB, lithium metal has received much attention as a promising negative electrode material. The interest in this material has arisen from its unique electrochemical properties. Lithium is the lightest and most electronegative metal (−3 V versus standard hydrogen electrode). The former makes it an anode of high specific charge (3,862 mAh g⁻¹). The latter leads to maximum cell voltage, when lithium metal is used in conjunction with any positive electrode material. However, lithium metal encounters severe difficulties in terms of cycle life and safety, which stem from its reactivity with the electrolyte and the extensive shape changes that occur after repetitive cycling [42, 43].

In Fig. 8, the historical trend of patenting activity on lithium metal and other common anode materials is shown. The search algorithm underlying this patent search is based on the combination of the IPC codes H01M10/52 and H01M10/525, which cover Li-accumulators as well as lithium-ion batteries, respectively, with the IPC code H01M4, which covers electrodes in general, and multiple keywords and IPC codes, describing the individual anode materials. It was necessary to include the IPC code H01M4 in this search since silicon is employed for further applications within the LIB. Otherwise, the patent search would lead to inaccurate results.

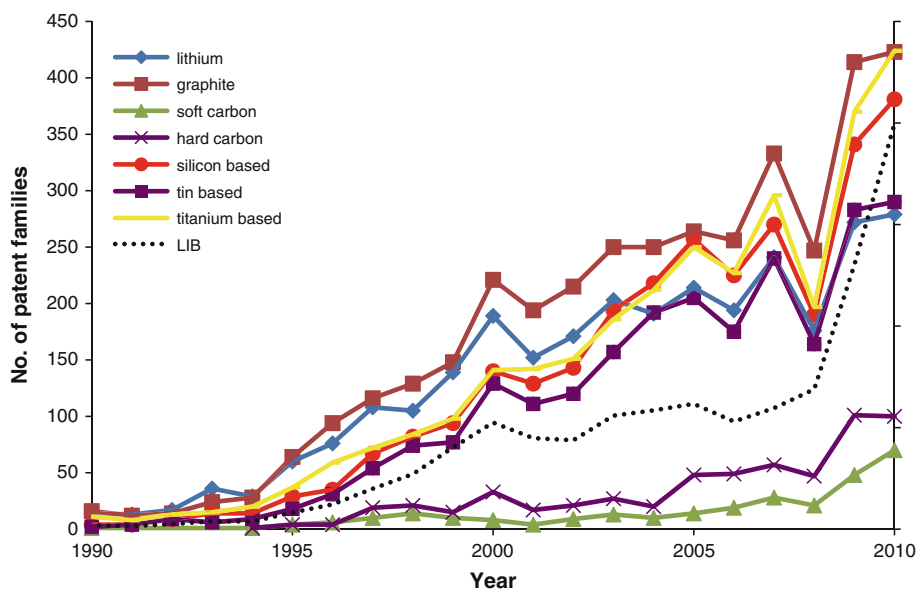
Lithium metal-based primary batteries became a commercial reality during the 1970s. A strong research effort to develop rechargeable LIB has accompanied the R&D of primary lithium batteries from their early stages. In the early 1980s, the first rechargeable lithium systems were introduced to the market [25]. However, patent activity at this time is still low. We therefore focus our patent analysis on the period up to 1990. According to the technological life cycle concept, lithium metal is found to be in the late maturity stage. The rate of growth as indicated by the average annual growth rate in the number of patent families for 2006–2010 has already start to slow down and amounts to only 9 %. Nonetheless, metallic lithium is still important as it is predominantly used as reference and counter electrode in battery tests.

Since the launch of the commercial LIB by *Sony* in 1991, carbonaceous materials, especially graphite, are predominantly used as anode materials. Figure 8 reflects the exceptional position of graphite as active material. By far, the largest number of patent documents has reference to graphite. The theoretical specific charge of graphite in the full charged state of LiC_6 is 372 mAh g^{-1} . Nowadays, the

practical specific charge of graphitic carbon used in LIB is close to this theoretical value, whereby Li storage is connected with very low potentials of 0.25–0.05 V versus Li/Li^+ [42]. Furthermore, graphite is inexpensive, easy to handle, and abundant as well as is characterized by good cycling stability and safety features [44]. One major drawback of graphite as an anode material is that the specific charge is limited to the relative low theoretical value of 372 mAh g^{-1} . Accordingly, the potential of further technological progress is restricted. This becomes obvious in the relative low average annual growth rate in the number of patent families for 2006–2010, which amounts to only 14 %. Nevertheless, it is generally accepted by the battery community, including the authors of this article, that graphite electrodes will remain the most important and relevant anodes in LIB in the near future, not least because they are used in new technologies such as dual-ion cells [45, 46].

In order to increase the specific charge of graphitic carbon, a variety of carbonaceous materials with different structural properties have been tested, since the crystallinity, the microstructure, and the morphology of the respective materials have a highly significant influence on the characteristics of the electrochemical intercalation reaction and determine the electrochemical performance of the active material [42, 47, 48]. Carbonaceous materials can roughly be classified as graphitic (materials with a layered structure) and non-graphitic (disordered). The latter can be further distinguished into graphitizing carbons, which develop the graphite structure during heat treatment, and non-graphitizing carbons, which show no true development of the graphite structure even at high temperatures. Since non-graphitizing carbons are mechanically harder than graphitizing ones, it is common to use the terms hard

Fig. 8 Historical trend of patent activity for the various negative electrode materials, as measured by the annual number of patent families. Source PatBase®, August 2012



and soft carbons, respectively. In the case of both, the soft and hard carbons heated below 800 °C, large specific charges up to nearly 1,000 mAh g⁻¹ could be obtained [49]. This high specific charge of non-graphitic carbons usually decays rapidly during cycling. Furthermore, these materials exhibit a hysteresis, meaning lithium uptake occurs close to 0 V versus Li/Li⁺, whereas lithium deinsertion occurs at much higher positive potentials. Hard carbons obtained at temperatures near 1,000 °C show little hysteresis. However, their high specific charge of several hundred mAh g⁻¹ can only be reached at a very low potential of a few mV versus Li/Li⁺, under which lithium deposition occurs [25, 42]. In the recent past, much effort has been concentrated on the development of these high specific charge carbonaceous materials. The average annual growth rates in the number of patent families for 2006–2010 for soft and hard carbon amount to 46 and 23 %, respectively, albeit both technologies are still in the emerging stage with regard to the technological life cycle concept. But, the high growth rates clearly indicate that carbonaceous materials will play an important role in the future. Owing to the structural variability, carbonaceous materials offer a vast playground for optimizing micro- and nanostructuring [50].

Since Dey already demonstrated in 1971 that metallic lithium can electrochemically alloy with other metals in liquid organic electrolytes, lithium alloys have been investigated during the past few decades [51]. Although these alloys provide a larger specific charge than graphite, they generally suffer from a large irreversible capacity at the first cycle and poor cycling behavior due to a large volume change of about 300 % during cycling [27]. Among the various Li-alloy elements, silicon attracted a great deal of attention since it can be lithiated up to a maximum stoichiometry of Li_{4.4}Si corresponding to a theoretical specific charge of 4,200 mAh g⁻¹ [52]. Besides, it is abundant, cheap, and environmentally friendly [53]. In order to suppress the Si volume expansion during cycling, various approaches have been applied such as Si dispersion in active and/or inactive matrices, Silicon–carbon composites and carbon coatings as well as SiO and its composites [54]. From 1995 onwards, the year in which *Fuji Photo Film Co., Ltd.* announced its Stalion[®] LIB—which employed an amorphous tin-based composite oxide (TCO) as the anode material—a strong increase in patent activity is obvious (cf. Fig. 8) [55]. A further increase in patent activity can be seen from 2002 onwards, when carbon-coated Si as well as SiO-based anodes were reported by Yoshio et al. [52] and Yang et al. [56], respectively. Since silicon alloys provide the highest gravimetric energy density for LIB and silicon is the second most abundant element in Earth's upper continental crust, they are among the most appealing and competitive materials for new

generations of negative electrodes [44, 53]. Its promising status can be seen as well in Fig. 8.

Beside silicon, tin is in the main focus as lithium alloying metal as its theoretical specific charge is about 990 mAh g⁻¹ (Li_{4.4}Sn) with an operating potential of about 0.6 V versus Li/Li⁺ [57, 58]. Since *Fuji Photo Film Co., Ltd.* showed that its TCO anode had a reversible specific charge more than twice to that of graphite much research has been devoted to Sn-based oxide materials and their composites [54]. The development in patent activity in the period up to 1995 is similar like in the case of silicon (cf. Fig. 8). However, like other Li-alloys, its commercial use is limited by its comparatively poor capacity retention due to mechanical degradation caused by large volume expansion during cycling, particularly during the first cycle. The average annual growth rates in the number of patent families for 2006–2010 for silicon- and tin-based materials have already start to slow down and amount to 14 and 13 %, respectively.

Transition metal oxides are the last class of anode materials in our study. Among them, titanium-based anode materials, most notably Li₄Ti₅O₁₂ (LTO), have attracted much attention due to their benefits which include excellent stability, arising from its highly reversible zero-strain Li insertion, as well as low costs, and being environmentally friendly. One of the greatest advantages of LTO is its high rate capability without electrolyte decomposition. LTO operates within the stability window of standard carbonate electrolytes, thus avoiding the reductive decomposition of the electrolyte solvents and leading to improved reliability and calendar life. LTO intercalates Li at 1.6 V versus Li/Li⁺. However, its limited capacity of around 160 mAh g⁻¹ and its high Li intercalation voltage makes this material almost irrelevant for the high energy density batteries required for EV applications [19]. Nevertheless, due to its other excellent properties, this anode material may be important for other applications, such as load leveling. In addition, LTO can serve as an important counter electrode for studies at the laboratory scale aimed at exploring the electrochemically behavior of new cathode materials without interference from the anode side [19, 54]. The patent search revealed that titanium-based materials are currently the materials with the highest competitive impact. These compounds have the second largest number of matching patent documents and have an average annual growth rate in the number of patent families of 18 % for 2006–2010 (cf. Fig. 8).

4.5 Electrolyte

A key issue related to the operation of LIB is the choice of the electrolyte [27, 59]. Most LIB available in the market utilize nonaqueous electrolyte solutions, where lithium

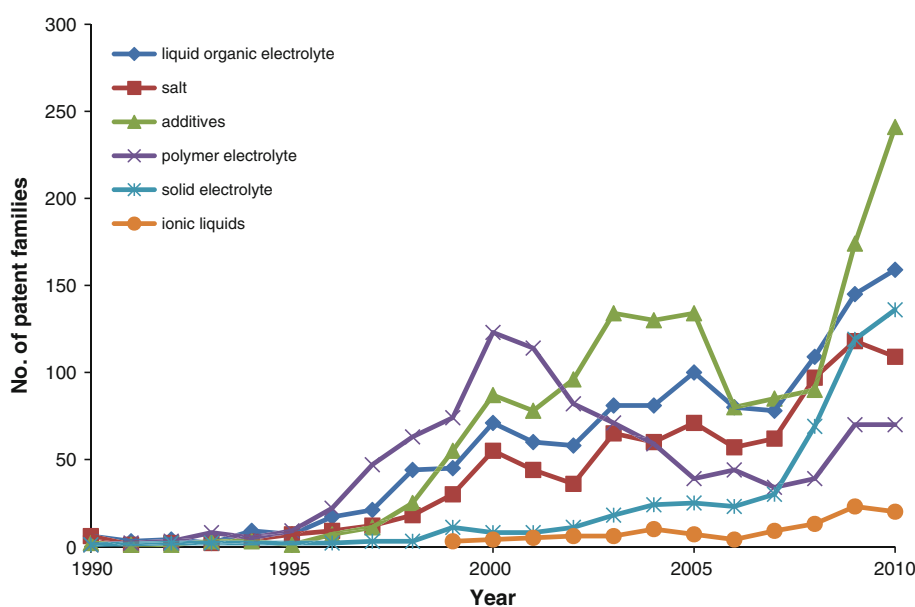
salts are dissolved in aprotic organic solvents. These mixtures have to fulfill the following requirements. As already mentioned in Sect. 2.1, the electrolyte in LIB acts as an ionic conductor to enable the shuttling of lithium ions between both electrodes. Thus, on the one hand, the electrolyte should be a good ionic conductor, leading to low internal cell resistance. On the other hand, a further requirement for the electrolyte is to have a high reductive and oxidative electrochemical stability, so that electrolyte degradation would not occur within the range of the working potentials of both the cathode and the anode. In addition to these essential requirements, further properties are important to ensure safety and inertness to other cell components to enable the operation over a wide temperature range as well as to meet environmental and cost challenges [60].

In Fig. 9, the historical trend of patenting activity on various electrolyte components is depicted. With the exception of ionic liquids, the search algorithm underlying this patent search is based on the combination of the IPC codes H01M10/52 and H01M10/525, covering Li-accumulators as well as lithium-ion batteries, respectively, with IPC codes, describing the individual electrolyte component. Owing to the limited depth of detail of the IPC classification, it was necessary to conduct the patent search with the use of multiple keywords in case of ionic liquids. This keyword search was conducted in the title, abstract, and claims of each patent document and was combined with the IPC codes H01M10/52 and H01M10/525 as well as H01M10/56, the latter one covering electrolytes in general, to reach better comparability.

At present, mixtures of alkyl carbonates including ethylene carbonate (EC) with one or more linear carbonates,

such as dimethyl, diethyl, and ethyl-methyl carbonates (DMC, DEC, EMC, respectively), and the Li salt, lithium hexafluorophosphate (LiPF_6) are used as electrolyte for LIB [25]. The alkyl carbonates are chosen due to their acceptable stability for the 4 V cathodes used in LIB, as well as lithiated graphite, together with other properties, such as high polarity, leading to good conductivity of the electrolyte, a wide liquid range defined by the difference between freezing and boiling point, sufficiently low toxicity, and acceptable safety features [61]. The exceptional position of liquid organic electrolytes is reflected in the continual increase in the patent activity since 1993, the year in which *D. Guyomard* and *J. M. Tarascon* reported DMC as a co-solvent with EC and LiPF_6 as a promising electrolyte for the first time (cf. Fig. 9) [62]. This new formulation of electrolytes based on a mixture of EC with a linear carbonate set the main theme for the state-of-the-art LIB electrolytes and was quickly adopted by other researchers and manufacturers [60]. However, with respect to the development of high energy LIB, focusing on the increase in its operating voltage using high voltage cathode materials such as high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, this state-of-the-art LIB electrolyte is not suitable. Cycling of LIB to high potentials (>4.5 V versus Li/Li^+) is always accompanied by significant oxidative decomposition of the conventional carbonate/ LiPF_6 electrolyte, resulting in relatively low coulombic efficiency and poor cycling performance [63, 64]. Accordingly, the potential of further technological progress for carbonate/ LiPF_6 electrolytes is restricted. The average annual growth rates in the number of patent families for 2006–2010 amount for both liquid organic electrolyte and salt to only 12 %, respectively

Fig. 9 Historical trend of patent activity for the various electrolyte components, as measured by the annual number of patent families. Source PatBase®, August 2012



(cf. Fig. 9). Nevertheless, in the recent years the R&D-efforts on new solvents, co-solvents, and salts are very promising [27].

The use of electrolyte additives is one of the most economic and effective methods for the improvement of LIB performance [65]. Hundreds of papers and patents are dealing with additives to electrolyte solutions, but a detailed discussion of such additives is beyond the scope of this paper. Our patent analysis confirms that electrolyte additives are the electrolyte components with the highest competitive impact. Additives have the largest number of matching patent documents and have an average annual growth rate in the number of patent families for 2006–2010 of 21 %. With regard to the technological life cycle concept, they are supposed to be in the maturity stage. Their promising status is also reflected in Fig. 9.

Polymer electrolytes have been studied for the application in LIB by many researchers to improve battery safety. In general, one can distinguish between two different types of polymer electrolytes. The first group includes pure polymer electrolytes, which are composed of a polymer matrix and a lithium salt. The second group encompasses gel polymer electrolytes, which are polymer gels containing electrolyte solutions. Pure polymer electrolytes show relatively low ionic conductivity. Therefore, they are of mere academic interest, with only remote prospects for their application [60]. On the other hand, gel polymer electrolytes have an ionic conductivity a little lower than that of organic electrolytes. Different types of lithium batteries using gel polymer have already been commercialized [25]. Looking at the development of the annual number of patent families, polymer electrolytes show a relative low competitive impact. They are supposed to be in the late maturity stage, where the potential of further technological progress seems to be restricted.

The use of solid electrolytes is attractive in terms of improving the safety issue and energy density of LIB since they provide high electrochemical stability. The main drawbacks related to the use of the solid electrolytes are their low ionic conductivities and preservation of good interfacial contact between electrolyte and electrodes [25, 66]. Nevertheless, these materials show the highest patent activity in recent years. The average annual growth rate in the number of patent families for 2006–2010 amounts to 48 %. It is supposed that they will play a key role within the electrolyte research sector during the next years not least because they are used in new promising technologies such as Li-air batteries [67].

Ionic liquids are a new type of electrolytes for LIB and have recently been widely investigated because of their merit of safety, including a wide electrochemical stability window, non-flammability, and low volatility. Their main drawbacks are high viscosity leading to poor wettability of

the porous active mass of the composite electrodes and their low ionic conductivity at low temperature as well as very high prices [27].⁵ Our patent analysis confirms that ionic liquids are a relative new technology still being in the beginning of the emerging stage, in which the future development is uncertain. The average annual growth rate in the number of patent families for 2006–2010 amounts to 38 % making them a promising new type of electrolyte for future applications.

4.6 Cell design

Dependent upon the way of packaging, three different cell designs of LIB exist—cylindrical, prismatic, and pouch type. In Fig. 10, the historical trend of patenting activity on these common cell designs is shown. The search algorithm underlying this patent search is based on the combination of the IPC codes H01M10/52 and H01M10/525, covering Li-accumulators as well as lithium-ion batteries, respectively, with IPC codes, covering cell housing and multiple keywords, describing the individual cell design.

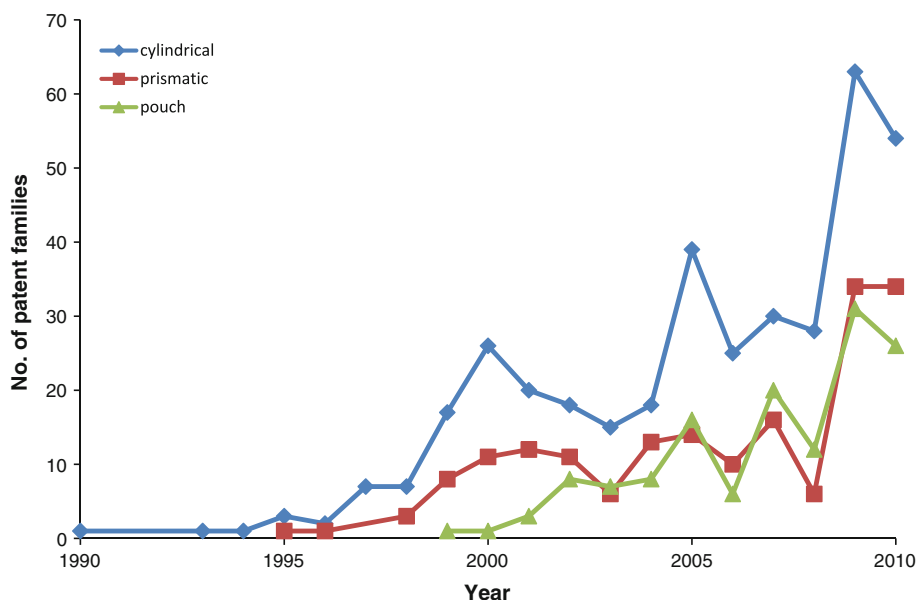
Cylindrical cells offer high energy density and mechanical stability, but do not use space very efficiently when assembled in battery modules. The most common design is the 18650 cell, whereas the number refers to the dimensions [69]. Our patent analysis reveals that the cylindrical design is the cell design most frequently used since it exhibits the largest number of matching patent documents.

Prismatic cells offer thinner geometry, which accordingly is their main advantage compared to cylindrical cells. They are most commonly applied in mobile phones [70]. Packaging of prismatic cells is easier, but manufacturing may be more expensive [69]. Prismatic cells have the second largest number of matching patent documents and have an average annual growth rate in the number of patent families for 2006–2010 of 87 %. The high growth rate makes them a promising design for future manufacturing.

Pouch cells avoid the use of metal casing. Instead they use an flexible aluminum foil to house the battery elements making the process of manufacturing much easier [70]. The main drawbacks are that they may swell during charging and discharging and have lower mechanical stability [69]. Moreover, when the pouch design is used, the cells are usually degassed and resealed after the first charge to enhance mechanical stability [71]. Pouch cells show the lowest competitive impact. They account for the smallest number of matching patent documents and have an average annual growth rate in the number of patent families for 2006–2010 of 54 %. According to the technological life cycle concept, cylindrical, prismatic, and pouch cell designs

⁵ For details see: [68].

Fig. 10 Historical trend of patent activity for the common cell designs, as measured by the annual number of patent families. *Source* PatBase®, August 2012



are supposed to be in the growth stage. In this scenario, the future development is still uncertain.

5 Conclusions

In this article, we conducted a patent search to give an overview on the patent landscapes within the field of LIB. We identified the current research trends and prospects for the main LIB materials and designs.

Our analyses of the generated patent sample revealed the increasing importance of LIB, becoming a major player within the energy storage sector during the next years. Both, the average annual growth rate in the number of patent families for 2006–2010 and the S-shaped technological life cycle concept indicate that LIB will play a significant role in the energy storage applied research in the future. Although the high growth rate may be surprising, our findings are consistent with literature [72].

Breaking down patent application growth by the different components of LIB shows the principal drivers of growth. Within the positive electrode materials, phospho-olivine compounds are the materials with the highest competitive impact; whereas titanium-based materials have the highest competitive impact among the negative electrode materials.

A key issue related to the operation of LIB is the choice of the electrolyte. Solid electrolytes are characterized by the highest patent activity in recent years. Therefore, it seems to be that they will replace the still very successful liquid organic electrolyte, salt, and additive mixtures in the future, not at least because they are used in new promising technologies such as Li-air batteries.

The cylindrical design is the cell design most frequently used since it exhibits the largest number of matching patent documents. Nevertheless, according to the technological life cycle concept, cylindrical, prismatic, and pouch cell designs are supposed to be in the growth stage, in which the future development is still uncertain.

Future research in the field of LIB should take advantage of these findings since the analysis of patent data in a technological area is regarded as a suitable and valuable forecasting tool. The identification of those materials with the highest competitive impact can help to ensure a more goal-directed research across different research laboratories in the future.

Future research focusing on patent data will have to explore all cell components by considering more detailed and revised analyses of the respective patent activity. Moreover, the constant improvement of the IPC-Classification system and in association to this, the feasibility of the employment of a more detailed search algorithm will lead to more entire datasets and therefore more specific bibliometric analyses will be realizable. Nevertheless, results from other publication analyses and prospects within literature should be compared to those obtained in this study for reasons of validation.

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