A review of the publication and patent landscape of anode materials for lithium ion batteries

Abstract

For a successful transition from internal combustion engines to electric vehicles and from conventional power plants to renewable energy supply, battery technology plays a vital role. Accordingly, battery research and development (R&D) efforts have been increased considerably over the past decades, particularly regarding materials and cell chemistries to further improve the electrochemical performance of lithium ion batteries. The impetus behind such massive R&D has been the replacement of metallic lithium anodes, a notorious for potentially catastrophic shorting by lithium metal dendrites. However, despite the promise of a step improvement in energy density outperforming established LIB technology, the commercial introduction of cells with alternative anode materials in the mass market is slow. Against this backdrop, the aim of the present study is to provide an overview of current developments in the academic and industrial research arena, summarising the historical development of scientific literature and patent landscape beyond established anode materials. The study identifies and critically reviews tin, silicon, silicon oxide, aluminium and titanium-based anode materials as promising pathways to develop high-energy density next-generation LIBs.

1. Introduction

For a successful sustainable transition, the development and further improvement of batteries is essential [1–3]. Accordingly, a tremendous research and development (R&D) effort is being carried out worldwide. Like data storage or processing power, battery technology has become a bottleneck for the use of renewable energies as well as the wide-spread deployment of electric vehicles [4–6]. After many decades of development, lithium-ion-battery (LIB) chemistry has taken the upper hand in the battery market for high performance applications due to the unique combination of lifetime, energy and power density [7–9]. Furthermore, the market success with the according mass scale production has triggered a rapid decline in price [8,10,11]. With the intention of overcoming the severe issues of lithium metal negative electrodes, carbon-based lithium intercalating materials were introduced and firstly commercialised by Sony in 1991. Starting with soft carbon (more precisely coke), a continuous improvement of this type of material has been achieved by hard carbon as well as graphitic carbon negative electrode materials [12,13]. This breakthrough was key for a broad-based commercialisation of this technology because lithium-metal based cells are notorious for catastrophic failure unacceptable for consumer products [14]. Interestingly, despite almost 30 years since their first commercialisation and even longer after starting R&D work on anodes, still to-date graphite is the almost exclusive anode material in lithium-ion battery cells [15]. Graphite has proven itself as cost-effective, safe and reliable material and competing materials are up for a major challenge to replace it [15].

The main motivation for finding alternatives for graphite-based anodes are their limited energy density as well as specific energy, which are rivalled by many other materials, namely silicon, tin or other lithium-alloying elements as well as by specific types of carbon materials like graphene or carbon nanotubes [16,17]. Especially, specific energy is for most alternatives significantly higher than graphite can deliver [18]. Despite the promise of a step improvement in energy density outperforming established LIB technology, the commercial introduction of cells with alternative anode materials in the mass market is slow [19]. However, there are prominent examples with significant amounts of Li storage metal/alloy materials as part of the anode that have been commercialised by established producers, *e.g.* the Sn-based Nexelion technology by Sony and a Si-based technology by Panasonic [20,21].

To shed light on this development, the present study aims at providing an overview of current developments in basic and applied research, summarising the historical development of scientific literature and patent landscape beyond established anode materials. For this purpose, a review of scientific publications and patents is presented, combining the historical development of scientific knowledge gain with the patent landscape for LIB anode materials. The comparison provides insights on which materials are considered promising as indicated by a rich scientific and patent literature.

The structure of the article is arranged as follows. Following this introductory note, section 2 presents the review of scientific literature on LIB, while the patent landscape is provided in section 3. Section 4 presents a comparative analysis of the publication and patent landscape as well as a discussion with regard to application. The study concludes with a summary of the main insights, enlisting limitations as well as opportunities for future research and development.

2. Literature review of LIB anode materials

2.1 Historical development, status quo and current challenges

LIB research had its first breakthrough in the 1970s, when Whittingham demonstrated the use of a titanium disulphide (TiS_2) cathode in a secondary battery with a lithium metal anode [22]. This was followed by further studies with Gamble, Besenhard and other colleagues on the intercalation chemistry for energy storage applications [23–28]. Between 1977 and 1979, Exxon marketed button cells for watches and other small electronic devices, consisting of LiAl and TiS_2 as anode and cathode materials respectively [29,30]. Further steps towards the commercialisation of rechargeable Li-based batteries, in particular lithium metal batteries (LMBs [31,32]) were made by Haering et al. using MoS_2 cathode and Li metal anode, which were later deployed in MoliEnergy battery cells. These batteries were rapidly recalled from the market due to safety-induced issues caused by lithium dendrite growth. In 1990, Dahn et al. developed a system using $LiNiO_2$ cathode combined with a carbon anode [33]. Nevertheless, the poor thermal stability of the $Li_{1-x}NiO$-phase and therefore a high safety risk hindered its final commercialisation.

With the implementation of Li_xCoO_2 as cathode material suggested by Goodenough et al. [34,35], Sony finally announced the first commercial LIB [36,37] using $LiCoO_2$ (LCO) cathode and a non-graphitisable carbon anode [38,39]. The replacement of the lithium metal anode by carbon is based on the pioneering intercalation work into graphite by Basu, Besenhard, Yazami, Armand and others, followed by Lazzari et al. and Base of Bell Laboratories [40–43]. Such insights have then contributed towards the development of a much safer chemistry, the LIB, due to a lower probability of high surface area lithium (HSAL [44]) formation by forming LiC_6. This is due to slightly higher voltage for Li^+ intercalation into graphite than the Li plating reaction on the Li metal electrode upon lithiation and therefore suitability for the mass market.

This breakthrough was a key driving agent for the mass commercialisation of graphite-based anode LIB technology, which from then on was in the position to compete with the currently available rechargeable battery cell technologies for portable applications, nickel-cadmium and nickel-metal hydride [45]. Interestingly, despite almost 30 years since their first commercialisation and even longer after starting R&D work on anodes, still to-date, carbon, particularly graphite, is the dominant anode material in LIB cells [15].

In general, most carbon materials show a well reversible Li^+ intercalation, whereas the quality and quantity thereof highly depends on various properties of the different materials, as for example the degree of crystallinity, structure, surface area, surface and bulk composition as well as morphology [46–55]. Many attempts have been made to optimise the electrochemical performance of carbonaceous materials, making use of complex nanostructures, pyrolysis of different precursors, surface modification, or *via* combining with high capacity materials. Carbon nanotubes (CNT) and nanostructured carbons in general have gained attention due to their high specific surface area [56], high electronic conductivity and improved ion diffusion [57]. But they also have drawbacks, such as high manufacturing cost [58], toxic residual metallic impurities [59,60] and high surface area, leading to irreversible electrolyte decomposition and thus the formation of a massive SEI layer. Owing to these drawbacks, the viability for commercialisation remains limited. Quickly after its discovery in 2004, graphene [61] became a widely investigated carbon-based material in battery research due to its unique physical and chemical properties [62–64]. In sum, graphite has proven itself as cost-effective, energy-efficient, safe and reliable material and competing anode materials are up for a major challenge to replace it [65,66].

Nevertheless, within the battery community, it seems to be well accepted that this development hits the ceiling reaching physical limits due to the rather moderate specific capacity of graphite with a maximum theoretical capacity 372 mAh/g, in regard to the unlithiated graphite mass and LiC_6 composition. The low capacity density of 787 mAh/cm^3 [38,39] and tedious optimisation strategies like reducing the electrode porosity and minimizing the share of non-intercalating materials [67] add to this. Reaching these chemical-physical limits has triggered the R&D work towards the development of higher-capacity, the so called “beyond” carbon intercalation materials, with metals and intermetallics being widely considered.

2.2 Promising new pathways

To enable the development of high-energy-density Li-ion batteries, the replacement of graphite by high capacity anode materials such as Li metal and alloying type anodes is one of the most imperative and promising strategies. However, the potential choice of metallic materials is vast. Due to the small size of Li^+ ions and its electrochemical activity towards alloying with other metals and intermetallics, numerous metallic host materials can reversibly store high capacities [68]. Nevertheless, for a functioning rechargeable battery cell, the alloying of lithium with the storage structure must be not only reversible at room temperature, but also at acceptable rates [69]. Moreover, other performance properties like costs, abundance, chemical reactivity, safety and a suitable redox potential versus $Li|Li^+$ need to be considered [70]. The search for such materials must facilitate a high energy density LIB since in most applications, space is limited. This long list of requirements brings down significantly the number of promising candidates.

For this paper, purposely chosen Li storage-type metallic anode materials are analysed in detail based on various parameters such as electrochemical performance, cost, toxicity, and safety-induced issues. While there exist various metallic and semi-metallic elements as well as compounds that form “alloys” with Li, this analysis will focus on tin (Sn), silicon (Si), silicon oxide (SiO_x), Aluminium (Al) and Ti-based anode materials, focusing on $Li_4Ti_5O_2$ and TiO_2. Other alloying-type anodes are not incorporated in the discussion for the above-mentioned reasons. For instance, the research activity on phosphorus and phosphides (P), bismuth (Bi), lead (Pb), and antimony (Sb) has remained low, ascribed to their instinctively high toxicity and/or high reactivity resulting in high safety risks [71–73]. Despite the high gravimetric (ca. 1,568 mAh g-1 and volumetric (ca. 2,300 mAh cm-3) capacities, the exploitation of Germanium (Ge) and its oxide (GeO_2) [74,75] are restricted due their high cost and toxicity.

In an attempt to examine the evolution of the research activity of anode materials for LIBs, publication data were obtained from Scopus, one of the leading citation and indexing databases. The reason why Scopus was chosen as data source includes its wider coverage of scholarly active journals (> 22,000), publishers (> 5,000), rich key words and a wide range of disciplines. The publication counts covered in the bibliometric data include original papers, and reviews. The research activity included spans from 1996 to 2019. The search term used in Scopus was “(lithium ion battery) and ((anode material) or (metal anode) or (metal alloy anode) or (intercalation anode))”. For Ti-based anodes, the sum of the two commonly investigated Ti versions, i.e., $Li_4Ti_5O_{12}$ and TiO_2 was considered.

As can be seen from **Error! Reference source not found.**, there has been a nearly exponential research activity increase on Si, (pure Si and/or carbon-doped Si), SiO_x, followed by Ti-based anodes (notably $Li_4Ti_5O_{12}$ and TiO_2), Sn and Al. For Si, 96% and 85% of the total publications were generated in the last ten (2009-2019) and seven (2013-2019) years respectively, once again testifying the capacious growth and accompanying emerging industry R&D interest. The impetus behind this weighty uplift could be linked to the huge interest emerging towards high capacity electrode materials. Besides the specific capacities and capacity densities, high abundance and thus low cost, high safety and a non-toxic nature are additional stimuli for the explosive research interest in Si and SiO_x materials.

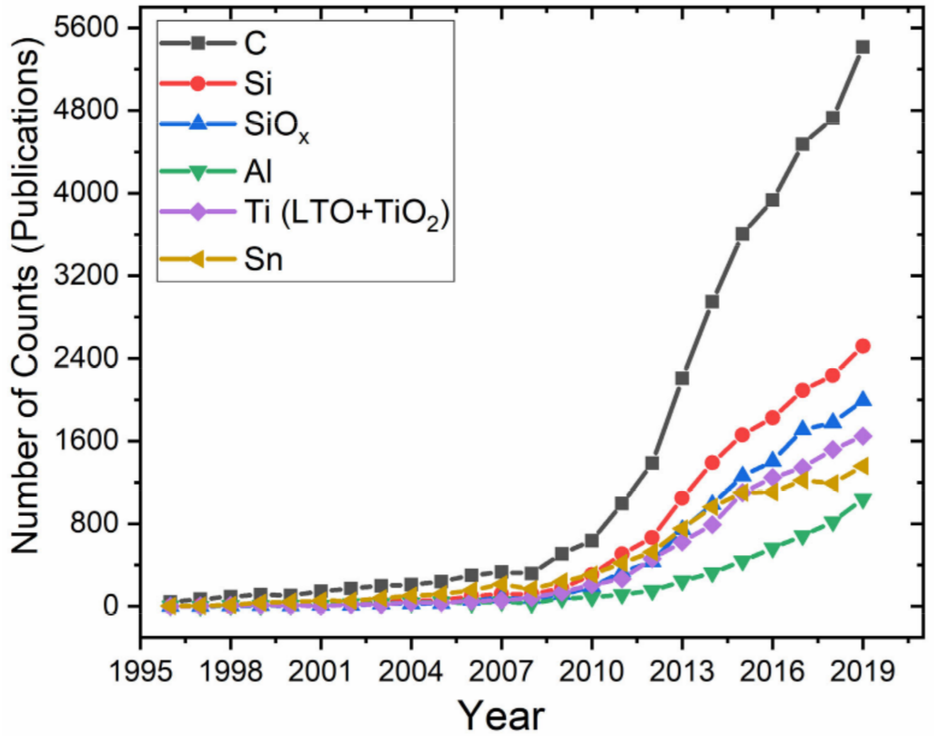


Figure 1: Evolution of publication activity of selected LIB anode materials

Figure 2 depicts publication activity on carbon families that are widely used as anode materials in LIB. Carbon families includes graphite, amorphous carbon, which include both soft (disorgered, graphitisable by thermal treatment at about 2300ºC) and hard (disordered, non-graphitisable) carbons as well as nanostructured carbons (graphene and carbon nanotubes). After 2010, publication activity on graphene, carbon nanotubes and graphite has been much higher compared to amorphous as well as soft and hard carbons. This could be related to their high irreversible capacity and safety issues.

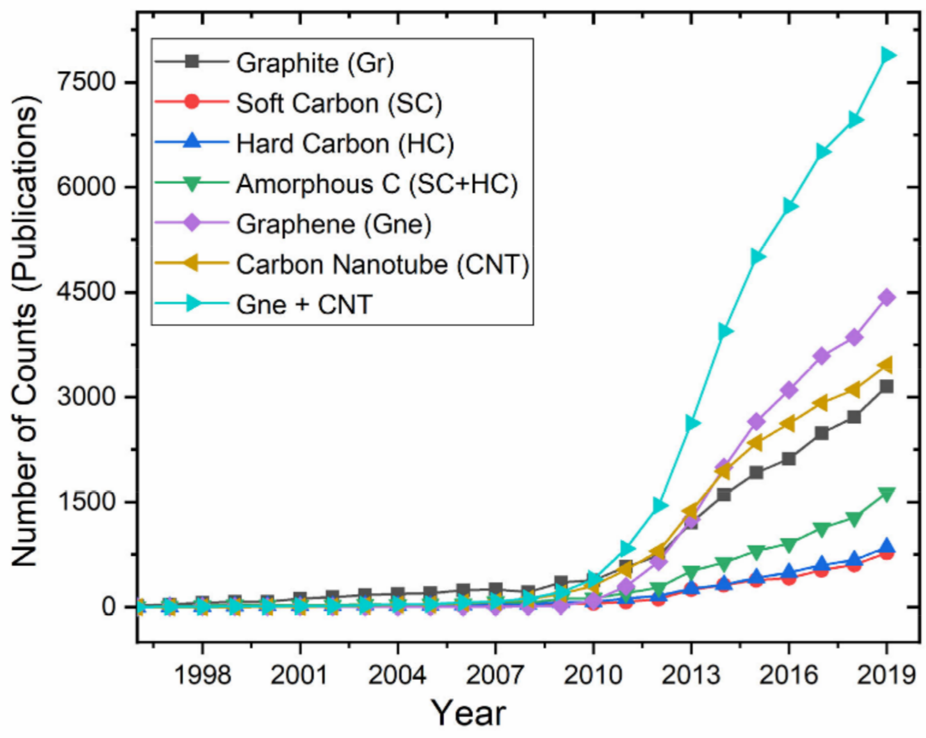


Figure 2: Evolution of research activity of carbon families.

Tin (Sn)-based anode materials have been hailed as promising materials for LIB applications. With a high theoretical gravimetric capacity of 992 mAh/g for the highest lithiated phases $Li_{22}Sn_5$ [19,76–78], tin is superior to graphite in this regard. The thermodynamics of the Li-Sn system were described by Foster et al. in 1966 [79], and since then, it has been the most researched alternative material (*i.e.* second after graphite) until 2007 (Figure 1). However, though tin-containing anode materials were commercialised by Sony in 2005 [80,81], the advent of the lighter storage host silicon (Si) resulted in weakening of the Sn-related research activities. Sony decided to withdraw the Sn-based anodes containing cells from the market due to shortened lifetime problems [82]. However, it is rather unclear whether cell manufacturers still make use of tin-based anode materials. The low abundance and thus higher raw material prices of Sn [66] and lower specific capacity (i.e. compared to that of Si) are ascribed as the driving reasons.

Silicon has a higher theoretical gravimetric capacity, but the capacity densities of lithiated tin (2020 mAh/cm^3) [78,83], and lithiated silicon (2400 mAh/cm^3) [84] do not differ that much. Moreover, unlike silicon, tin shows a high electronic conductivity and thereby enhanced rate capability [85]. Nevertheless, both, Sn and Si suffer from severe volume changes upon lithiation and delithiation. The volume increases of up to 300% for Si during the lithiation, which causes immense mechanical stress at the material and the electrode levels, which can further lead to cracking and subsequently pulverisation and contact loss of the active material to the current collector. Along with the cracking comes a dynamic solid electrolyte interphase (SEI [86,87]) film, which will break and reform upon cycling. Ultimately, this results in an ongoing electrolyte decomposition and therefore Li^+ consumption, electrode swelling and electrolyte drying [88,89]. Numerous strategies were developed to overcome these issues. Many efforts were made to synthesise nanoparticles and all kind of nanocomposites to decrease the impact of the volume changes on the electrode [90–95]. Creating void spaces, a porous structure to accommodate the extra volume can also improve the electrochemical performance [94–100]. Another way to buffer the volume changes is to prepare intermetallics (“alloy hosts”) [94,95,101–110] and other kinds of host matrices [90,111–113].

SiO_x-based anode materials have recently been explored as promising substitutes for elemental Si, attributed to their extremely abundant reserves, low cost, easy synthesis, smaller relative volume change [114] (approx. 200 % for SiO_x [115] vs. approx. 300% for Si [116]) during cycling due to the less amount of active Si, compared to pure Si. However, their practical application is hindered due to the intrinsically low electronic conductivity, low initial Coulombic efficiency and large volume change with respect to practicality [16,117]. Hence, despite the tremendous research efforts (Figure 1), the development of SiO_x-based anode materials is still in its infancy. Amid others, SiO and Si-rich SiO_x are relatively close to commercialisation. To meet the Coulombic efficiency requirement (>> 85% in full cells), the development of tailored electrolyte additives, designer polymeric binders and implementation of feasible, scalable and controlled pre-lithitation technologies should be developed and accordingly applied.

Lithium-aluminium alloys received plenty of attention in the early years of rechargeable LIBs [16,29,118,119] due to their high theoretical capacity (993 mAh/g for LiAl), similar to the highest lithiated Sn-phase $Li_{22}Sn_5$ [76], but with a lower volume expansion during lithiation (ca. 97% [120] instead of up to 300% for Si [78]). Additionally, aluminium as the most abundant metal in the earth crust and low in cost has a very high electronic conductivity [121] and a low potential plateau for lithiation (0.19 to 0.45V vs. $Li|Li^+$) [122]. Aluminium anode material suffers from a number of challenges. This includes the immediate oxidation, which forms a thick electronically and ionically insulating [123] alumina layer (Al_2O_3) on the surface, which requires its removal before application as LIB anode [124]. Another critical challenge is the large volume variation (≈97% for Li_9Al_4 compared to ~10-12% for graphite) during the Al–Li alloying/dealloying process [125]. To overcome these disadvantages and to emphasise the advantages of aluminium, many scientists proceeded their research for example by combining Al with carbons [126,127]. Stand-alone Al anodes further suffer from pulverisation despite using nanosized material e.g. nanowires [123] and therefore need to be embedded in a buffer matrix.

In the early 1980's, Murphy et al. were one of the firsts to investigate the lithium insertion of various TiO_2 polymorphs, forming Li_xTiO_2 [128]. Since then, the interest in Ti-based anode materials has been increasing, especially because most of them show minor to zero (for $Li_4Ti_5O_{12}$, LTO) volume change and thus structural change (zero-strain material) [128–130] and therefore exhibit a good cycling reversibility. Additionally, these materials are of low cost, non-toxic and exhibit an improved safety due to high operation voltage [131]. No advantage comes without disadvantages and TiO_2 is no exception. A large polarisation at high rates deprives the rate capability [132]. Slow ion diffusion [133] and poor electrical conductivity [134] require further improvement, employing strategies such as doping, surface modifications and utilising nano-sized materials [132]. Among the different polymorphs and Li-Ti-O phases, $Li_4Ti_5O_{12}$ seems to be most promising candidate with a theoretical specific discharge capacity of 175 mAh/g, corresponding to $Li_7Ti_5O_{12}$ (accommodation of three Li^+) [132]. The volume change upon lithiation is 0.2%, negligible compared to other alloy-type anode materials [135,136]. However, the low electrical conductivity ($\sim 10^{-13}$ S cm^{-1}) of $Li_4Ti_5O_{12}$ [137] requires further modification involving doping and other approaches which are capable of drastically improving it [138,139]. Going to microscale or even nanoscale shortens ion diffusion pathways by increasing the surface area and reducing particle size resulting in an improved kinetics [140,141]. A similar effect can be obtained by using hollow structures, whereas in this case, the enhanced electrode-electrolyte contact is more decisive [142]. These principles are not just valid only for $Li_4Ti_5O_{12}$ but also for all other polymorphs. Among all TiO_2 polymorphs, namely anatase (tetragonal, I41/amd), rutile (tetragonal, P42/mnm), brookite (orthorhombic, Pbca) and synthetic forms like e.g. TiO_2-B (monoclinic, C2/m), rutile is the most thermodynamically stable. In literature, good electrochemically performance was only reported for Li_xTiO_2 with low lithiation degrees ($x < 0.5$) [143], while higher lithium amounts lead to irreversible structural changes.

3. Patent landscape of LIB anode materials

3.1 Method and data

To include and combine insights from industrial and industrially relevant R&D, patenting activity concerning the above-mentioned anode materials for the application in LIBs is analysed to complement scientific publications. Patent analysis can provide insight into the early stages of technological development and market potential [144]. Patents are furthermore a frequently used measure for technology forecasting as they reflect current technological developments and trends [145–147].

PatBase is used for patent data collection. PatBase is a global patent database, which includes more than 57 million patent families filed from over 105 institutions. Patent families include all patents related to a particular invention, avoiding duplicates and thus increasing the value of the results [148]. It should be noted that there is a time lag in patent statistics caused by an 18-months patent disclosure timeframe [149] and thus, all relevant patents up to and including 2018 could be taken into account for the present analysis.

The patent retrieval took place in October 2020 via a combined search approach using keyword combinations partly adapted from Mueller et al. [150] as well as International Patent Classifications (IPC) (see Appendix 1). Not before 1991, when Sony began to commercialise LIBs, the term “lithium-ion battery” was established. We therefore had to broaden the patent search for the period before 1991 by omitting the term “lithium ion battery” and manually checking inventions related to the anode materials considered in this review.

The data set is analysed using a three-step approach. To provide an overview of the historical developments, patent activity over time is analysed in the first step. In step two, the most active assignees add insights on the industries driving anode material R&D. On this basis, the third step zooms into the proportion of university R&D, allowing further insights on the drivers of anode material R&D.

3.2 Development of patenting activity over time

The development of patent applications for anode materials used in LIBs over time is illustrated in Figure 2. From the curve progression, three phases can be identified in the development of patent families over time. Phase 1 between 1960 and 1991 is characterised by very limited patenting activity. Phase 2, up until 2009, shows a surge in patenting activity on varying levels for all selected materials. In the final phase 3, comprising the last decade between 2009 and 2019, patenting activities for different materials not only occur on different levels of intensity, but also show diverging developments from exponential growth to plateaus and slow decline.

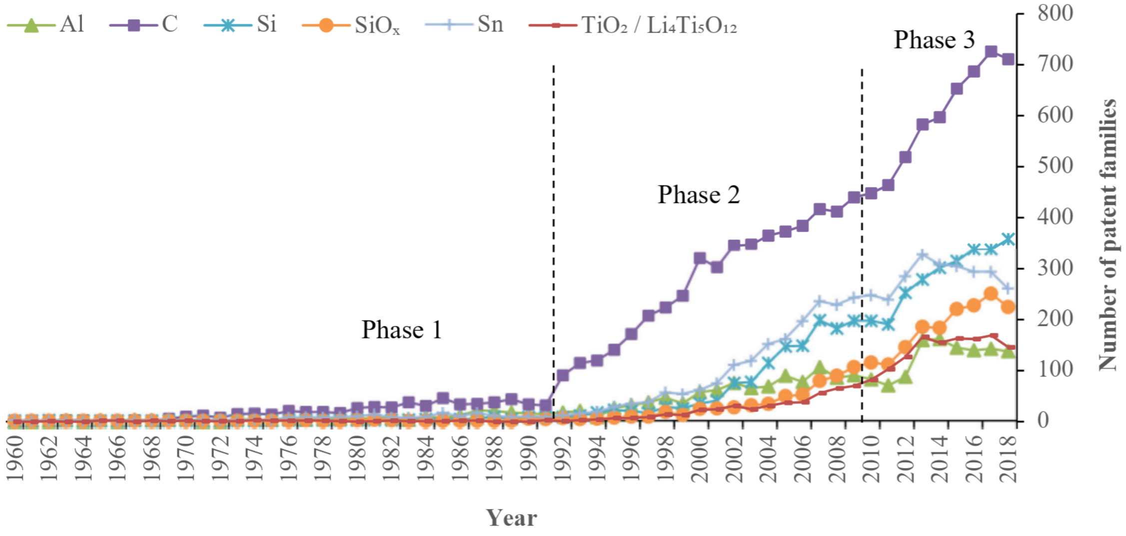


Figure 2: Development of patent families for different anode material in LIBs.

Phase 1 spans from the first patent in 1966 until the initial commercialisation of LIBs in 1991. Although prior to commercialisation of LIB secondary cells, primary Li cells were already successfully commercialised in the 1970s and are still used today for niche applications [151–155]. Apart from the slowly rising activity for carbonaceous materials, initial efforts can be observed for Sn- and Al-based materials.

Phase 2, spanning over almost two decades between 1992 and 2009, is shaped by a sharp increase in patenting activity. From 1991 onwards, the number of newly filed patent families for carbonaceous anode materials increased steadily over a period of about 10 years, to more than 400 applications per year. From 1998 onwards, patenting activity of other anode materials has also been discernible. Tin- and silicon-containing materials show a steeper increase, followed by SiO_x, Ti and Al-based materials. The latter alternative materials show a flatter increase and stabilise at around 100 patent families per year between 2007 and 2011, while tin- and silicon-based materials shortly plateau around 200 patent families per year. Such a shorter period of stable or even declining activity is not unusual in the life cycle of technologies and can be attributed to a necessary consolidation of the previously strong growth across all materials (Ernst 1997).

This consolidation marks the transition into phase 3. Patenting activity regarding carbonaceous materials grows at an even faster pace compared to phase 2 and still dominates the patent landscape. While Si-based materials have been following Sn-based materials as a close second alternative throughout phase 2, Si overtakes Sn-based materials in 2015 to now rank second behind carbonaceous materials. SiO_x-based materials also gained ground and were able to offset from Ti- and Al-based materials starting from 2014. While Al already reaches peak activity in 2014, C, SiOx, Sn and Ti show the highest number of yearly patents in 2017. In fact, the only material that does not show a decline in patenting activity in recent years is Si.

3.3 Most active assignees

Due to non-existent large-scale commercial use of LIB cells in phase 1, the patenting activity before 1991 is low, but nevertheless has generated ground-breaking and influential patents (**Error! Reference source not found.**). Secondary cells using Li-metal as anode active material have been developed with intensive research effort by e.g. Exxon 1978, Hitachi 1979, Duracell 1981-1985, and Bell Lab 1983-1986. Japanese and US companies are the most active assignees in this phase (Appendix 2a). However, these cells had to be withdrawn from the market primarily due to HSaL-driven safety and cyclability issues [156,157]. Another well-known example was the Li metal battery commercialised by Moli Energy in 1985 under the name Molicel. A few years later, in 1989, these batteries had to be withdrawn from the market due to multiple fire incidents [158,159]. Therefore, phase 1 is labelled the *LIB pre-commercialisation era*.

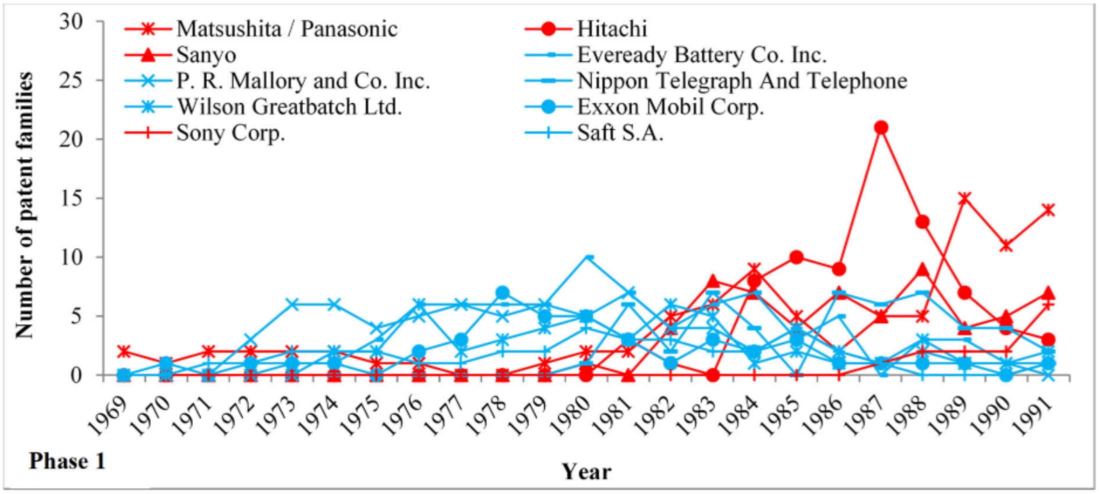
Table 1: Selected important patents related to anode materials and lithium-ion batteries before 1991.

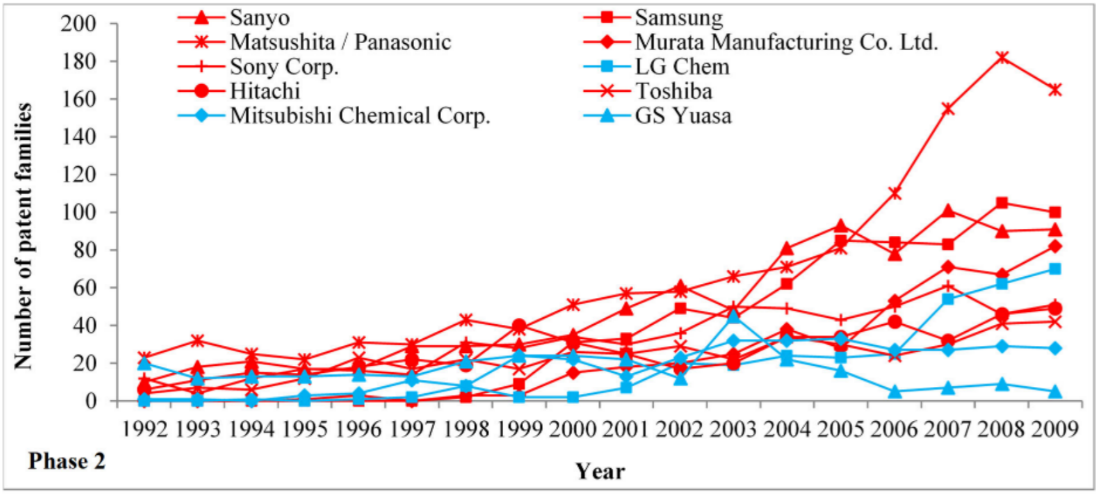
Patent	Patent No. and application date	Family No.	Inventors	Assignee
Rechargeable cell with light metal anode alloyed with Lithium – and anhydrous electrolyte containing corrosion inhibitor forming insoluble Lithium compound	DE2834485C2, 07/08/1978	1734009	Heinz Fritz, Jürgen Besenhard	Rheinisch Westfälisches Elektrizitätswerk AG
Lithium Battery	JP55124962, 19/03/1979	1561111	Hironosuke Ikeda, Satoshi Narukawa, Shigemaro Nakaido	Sanyo Electric Co.
Lithium molybdenum disulphide battery cathode	US4224390A, 30/08/1979	30148581	Rudolph R. Haering, James A. R. Stiles, Klaus Brandt	Moli Energy Ltd.
Ambient temperature rechargeable battery	US4423125A, 13/09/1982	3887149	Samar Basu	Bell Telephone Laboratories Inc.

Secondary Battery	JP1989293C3, 10/05/1985	24045806	A. Yoshino, K. Sanechika, T. Nakajima	Asahi Chemical Ind.
Non aqueous electrolyte secondary battery	JP2943287B2, 04/09/1990	30341331	T. Ogino, K. Takagi, T. Kawagoe	Bridgestone Corp.
Non aqueous electrolyte cell	US4959281A, 25/09/1990	11900631	H. Azuma, T. Komaru, M. Nishi	Sony Corp.

In phase 2, the technological activity was of moderate academic interest and driven forward by leading electronics companies (e.g. Sony, Samsung, Sanyo and Matsushita, in recent years as Panasonic) aiming at applying LIBs for their respective products (Figure). This has caused a shift to Japanese and South Korean based companies being the most active assignees (Appendix 2b). Therefore, incremental efforts for anode materials primarily driven from industrial R&D led to the emergence of carbon-containing anode materials as well as to the introduction of alternative anode materials like tin, silicon or aluminium for industrial applications. On this basis, phase 2 can be described as the *Rise of LIB as enabler technology for the electronics industry.*

Considering the period from Figure emanating from 2010 until present, increasing patent activity can be observed from companies that are not primarily associated with the electronics industry. Specifically, companies from the automotive and chemical industry can be found, which indicate forward and backward integration along the battery value chain [160]. The Japanese and South Korean dominance prevails, with Robert Bosch GmbH as a German-based company being among the most active assignees (Appendix 2c). This is an indication for the transition of LIB technology to the application in new fields and thus induces an increased attractiveness for supplying industries. As one example, BASF, the world's largest chemical company, invested in R&D projects for cathode materials used in LIB back in 2005 [161] and is today a renowned cathode active material supplier to battery cell producers for electrified vehicles around the world [162]. The last phase 3 can therefore be associated with the *Diversification of LIB into different application contexts*.


Number of patent families
30
25
20
15
10
5
0
Matsushita / Panasonic
Hitachi
Sanyo
Eveready Battery Co. Inc.
P. R. Mallory and Co. Inc.
Nippon Telegraph And Telephone
Wilson Greatbatch Ltd.
Exxon Mobil Corp.
Sony Corp.
Saft S.A.
1969 1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991
Phase 1
Year


Number of patent families
200
180
160
140
120
100
80
60
40
20
0
Sanyo
Samsung
Matsushita / Panasonic
Murata Manufacturing Co. Ltd.
Sony Corp.
LG Chem
Hitachi
Toshiba
Mitsubishi Chemical Corp.
GS Yuasa
1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009
Phase 2
Year

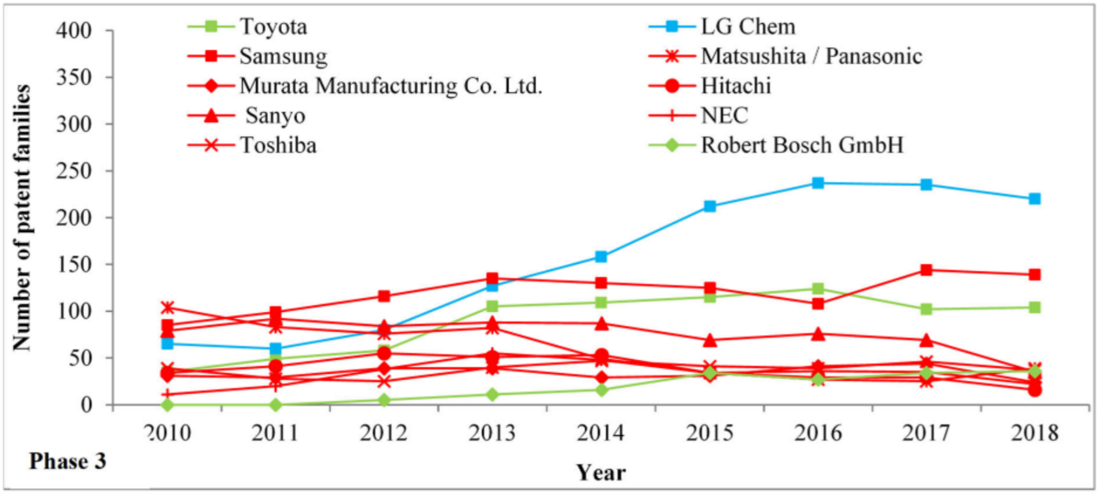

Number of patent families
400
350
300
250
200
150
100
50
0
Toyota
LG Chem
Samsung
Matsushita / Panasonic
Murata Manufacturing Co. Ltd.
Hitachi
Sanyo
NEC
Toshiba
Robert Bosch GmbH
2010 2011 2012 2013 2014 2015 2016 2017 2018
Phase 3
Year

Figure 4: TOP 10 applicants' development of patent families regarding anode materials for application in LIBs over time, structured according to phases 1 to 3, with industry-specific colour coding (red shades for electrical industry, green shades for automotive industry, blue for chemical and other industries).

3.4 The role of university R&D

The last step of the patent analysis aims at identifying the share of university R&D in driving the development of anode materials. For this purpose, patent assignees for the individual materials are analysed, particularly distinguishing between industry companies (industry in the following) and universities or public research institutions (universities in the following). The shares of patents applied for by universities over the three periods are presented in Figure 5. Not surprisingly, the majority of patenting activity is carried out in industry. It is striking though how the share of university patents has grown over time from zero or very low single digits to between 11 and 17%, reflecting the increase in research activity as well as the awareness of researchers regarding the impact of their work. The most influential universities, measured by the number of forward citations, are presented in Figure 6. Four of the universities are based in the United States (US), with California Institute of Technology leading the field with double the number of citations compared to Massachusetts Institute of Technology (MIT) as the runner-up. Three Korean research institutes play an important role, while one university each comes from China, Israel and Taiwan.

With the exception of Ti and SiO_x changing places (four and five), university patents show the highest share for materials with the highest overall patenting activity. It is noticeable that the share of university patents for Si-based materials almost equals carbonaceous materials, although carbonaceous materials show significantly higher overall publication and patenting activity (Figure 1 and Figure 3).

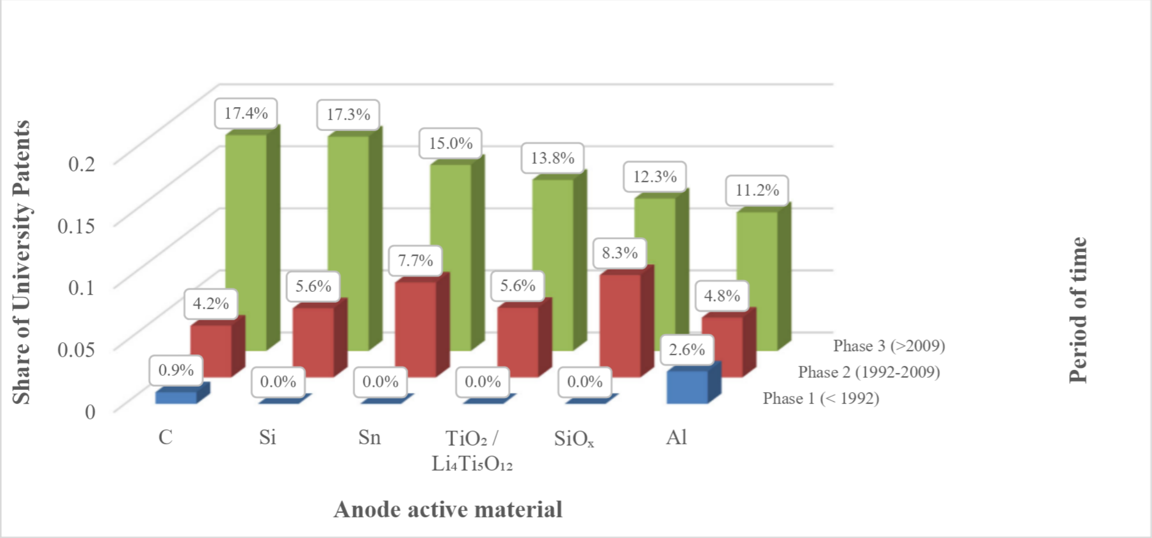


Figure 5: Share of patent families on various anode materials for LIBs, applied by universities and industry.

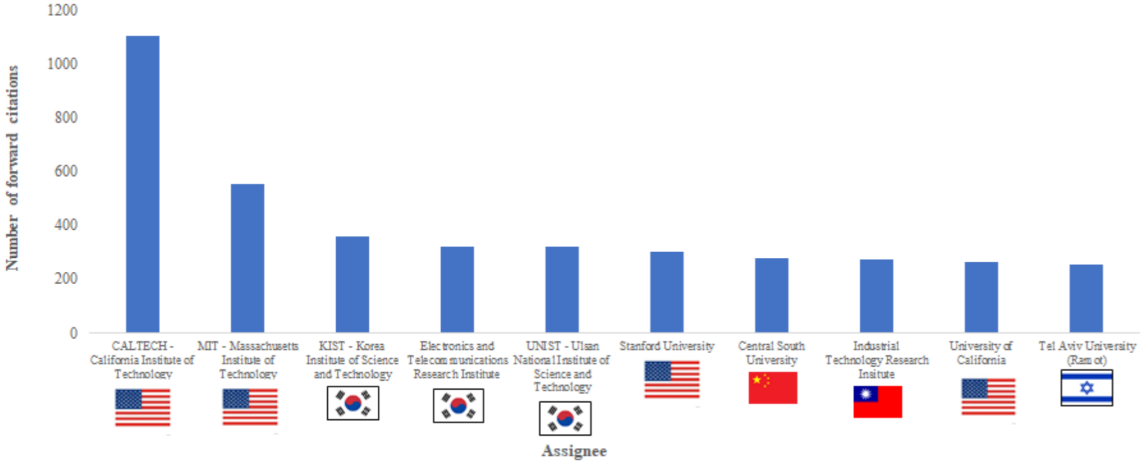


Figure 6: Most influential universities and research institutions patenting in the area of anode materials for LIBs based on forward citations.

Carbon (C):

Although carbonaceous materials are the most technically mature, the share of university patents is the highest of all materials with more than 17%. This emphasises the rich possibilities of synthesis and complexity due to a wide range of morphologies and according electrochemical properties including carbon nanotubes as well as graphene and their variations [38,39,163,164]. For example, the ability of fast charging/discharging versus capacity of carbonaceous materials can be tuned in a wide range. Even more so, charging capacities for carbon allotropes such as carbon nanotubes and graphene can outnumber state of the art materials like natural graphite. Nevertheless, for industrial application, a facile and low cost synthesis is desirable and one may therefore question whether the energy-intensive production of carbonaceous materials may have reached its limit [67].

Silicon (Si):

Despite its more recent history of usage in LIBs compared to carbonaceous anode materials, Si-containing anode materials have an almost equal proportion of university patent applications. Compared to the ratio in scientific publications, the share of patents regarding Si is over proportional. These findings may indicate that Si-containing anode materials are considered as most likely to be implemented in commercial applications. This is emphasised by the fact that Si is the only material where patenting activities are on the rise. This is in accordance with several announcements by Asian cell suppliers of high-energy LIB cells with silicon-modified carbon/graphite electrodes. The announcement of Tesla Inc. that silicon plays a role in their current battery cell may have intensified activities amongst competitors [165]. It appears likely that the percentage of silicon as part of blend electrodes will increase with improved scientific understanding of degradation and the development of mitigating strategies to stabilise Si-based anodes [15,166,167]. Such practical implementation of silicon in commercial cells will most likely trigger more work on such materials just as the introduction of graphite in commercial cells in 1991 by Sony has triggered phase 2 of the development – a large increase in activity and rising interest in the research community.

Tin (Sn):

Tin-containing anode materials have a slightly lower share in patent applications from universities of around 15%. This class of materials has receded somewhat into the background in academia (scientific publications and patent applications) as well as in industry following the market withdrawal of Sony's Nexelion cells [82] and increasing research activity on Si-containing materials. However, with its chemically similar properties to silicon, some of the progress being made on silicon materials might be applied to Sn, which may offer alternative roads for Sn as anode material.

Titanium (Ti):

With regard to the temporal development of patent families, titanium-containing anode materials play a subordinate role. However, the proportion of university patents with close to 14% is not too far away from the three leading materials mentioned above, indicating intensified academic research interest. This is further substantiated by the fact that current studies are often limited in terms of focusing on half-cells, while disregarding full cells [168,169] as well as not presenting coulombic efficiencies, which are important key factors on the way to practical application.

Silicon Oxide (SiOx)

In absolute numbers of patent applications and scientific publication, SiO_x has received less attention than Si. One of the reasons might be that the high initial irreversible capacity losses renders it a less promising material than Si despite the fact that the volume variations during charge/discharge are much less severe. However, when pre-lithiation [50,170,171] is applied to overcome the high irreversible capacity losses, the use of silicon oxides as anode material is promising for applications in product lines due to a number of additional beneficial features such as lower volume change, high abundancy of reserves, low cost and easy synthesis and processing.

Aluminium (Al):

Al-containing materials show the largest involvement of universities in phase 1, although on a low level of just above 2.5%. The abundant availability and a well developed industry processing aluminium on a large scale made it an attractive target for battery research. Despite the growing patenting activity over time, Al is the material with the lowest share in university patents in phase 3 of about 11%. This aligns with previous findings highlighting Al as the material with the lowest level of overall publication and patenting activity. In addition, Al-containing anode materials are mentioned in patents as a complementary rather than main material. In accordance with fundamental material-specific chemical difficulties, e.g. slow ion diffusion [65], this result may indicate that neither university nor industry R&D considers this material to be particularly promising for achieving higher energy densities and practical endurance. Nevertheless, with regard to scientific curiosity, materials with multi-dimensional ordered structures are an attractive option and might lead to a step-improvement in battery technology, initially appearing in niche applications with highest demands on energy density and lowest cost pressure. One particular challenge for the scientific research community in this respect is the illumination of the particularly slow lithium diffusion and the irreversibility of the alloying process.

4. Conclusions

Considerable progress has been made in LIB R&D over the past decade to find alternatives for graphite-based anodes due to their limited energy density as well as specific energy. Despite a range of potential alternative anode materials promising to outperform established LIB anode technology, the commercial introduction of cells with alternative anode materials in the mass market is slow. Against this backdrop, this review provides an overview of the current developments in the academic and industrial research arena, combining the historical development of scientific knowledge gain with the patent landscape beyond established anode materials. Based on the analyses of scientific publications and patenting activity, this review reveals the following main insights:

1. Carbonaceous materials are still and beyond doubt the dominant anode active materials applied in LIB. This is emphasised by an extensive number of scientific articles and patents, with publications dating back to well before the commercialisation of LIB in 1991. However, patent activity peaked in 2017, which may reflect the maturity of the material in terms of research and application leading to less opportunities for patentable innovation. It is also notable that scientific work on CNT and graphene nano-materials has seen a large boost starting around 2010. Nevertheless, the commercial battery cell market is still dominated by hard and soft carbon materials stressing that obstacles like costs, availability as well as technical challenges remain high for highly promising, yet academic

nano-materials. This also indicates a detachment of hypes in academic research from industrial realities.

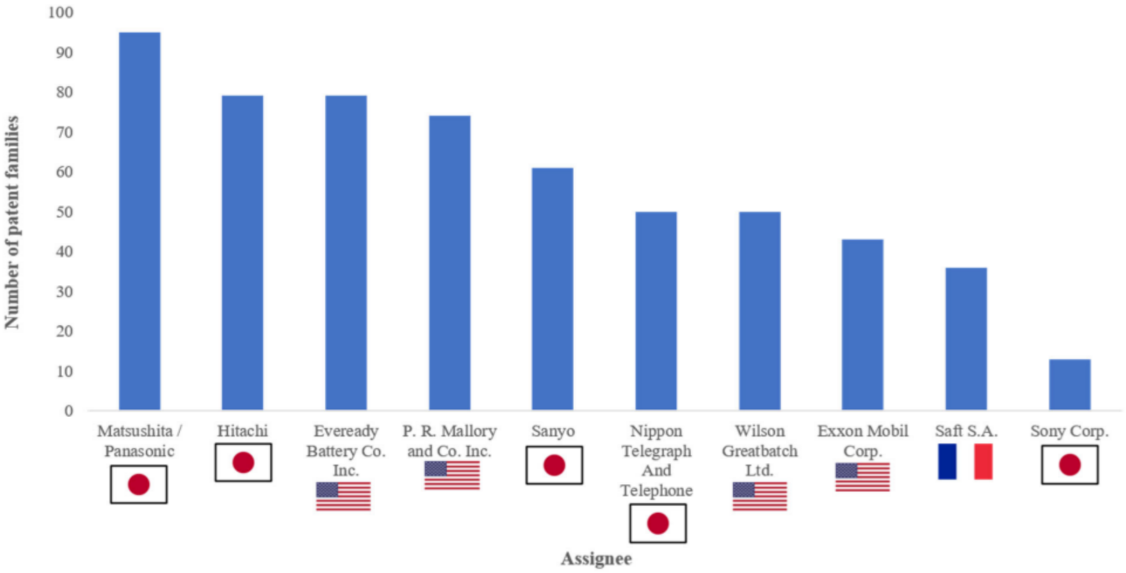
2. Tin, silicon, silicon oxide, aluminium and titanium-based anode materials are promising pathways to develop high-energy density LIB. Sn- and Si-based materials are the most studied alternatives, while SiO_x-, Ti- and Al-based materials follow close behind. The only material that does not show a decline in patenting activity in recent years is Si, even overtaking Sn-based materials to now rank second behind carbonaceous materials. It appears that industry and academia consider Si as the most promising material to boost LIB as drop-in technology when blended with carbonaceous materials.
3. Three phases in anode material R&D could be identified: Phase 1, the "LIB pre-commercialisation era" until 1991, phase 2, the "Rise of LIB as enabler technology for the electronics industry" until 2009 and phase 3, the "Diversification of LIB into different application contexts". The analyses give clear indication that Si has become the major contender for enhancing LIB capacity for mass market applications. Other elements have fallen behind and there is no indication that Sn or Al are currently being introduced in commercial products. On the other hand, in commercial battery cells only few percent of Si are being found in graphitic blend anodes, which points at the fact that there are still major obstacles in terms of lifetime and reliability when increasing the Si amount. This gives rise to a large space of opportunities for industrial R&D with room for breakthrough innovation.
4. Overall, the patent and research landscape for anode materials is overwhelmingly large and has been expanded by the prospects of mass market adoption. University R&D has been following this trend swiftly and a few main roads of development have been identified with carbonaceous and silicon materials in the lead. Other materials like Al have fallen behind and no indication of adoption in applications can be seen at the horizon at the moment. This indicates that fundamental issues have either not been solved or there are obstacles not to be overcome. This can be taken as a motivator for academia to more fundamentally explore the properties of lithium alloying and de-alloying as well as finding ground-breaking new material morphologies. This could be a potential space for ground-breaking scientific work going beyond the application-focused industry R&D.

Appendix

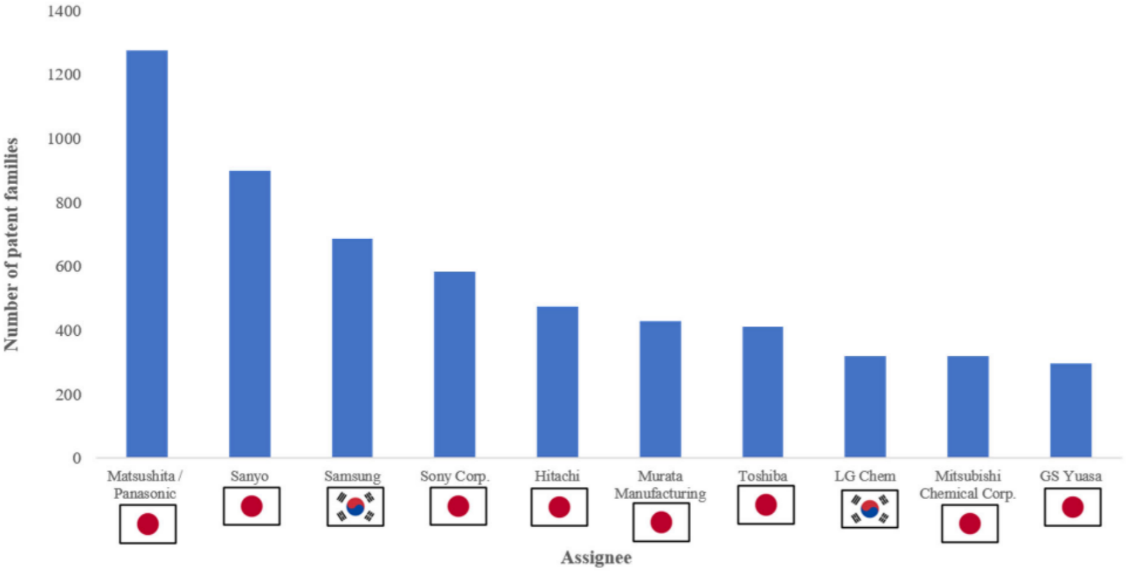
Appendix 1. Applied search terms for patent data retrieval.

Anode material	*Search term*
Al containing	STA=(anode OR (negative AND (electrode OR active material OR pole material))) NOT TI=(cathode OR (positive AND (electrode OR active material OR pole material))) AND SFT=(lithium or lithium-ion or (lithium w5 ion) w5 (cell% or secondary batter* or batter* or accumulator)) AND STAC=(Al OR Al2O3 OR alumin*) NOT STA=((Al OR alumin*) w5 (container OR shell OR cladding OR foil OR collector OR sheet OR disc)) NOT CC=(IT OR ES) AND IPC=(C01F7* OR H01M4/131* OR H01M4/134 OR H01M4/1391* OR H01M4/1395 OR H01M4/46 OR H01M4/48*)
C containing	STA=(anode OR (negative AND (electrode OR active material OR pole material))) NOT TI=(cathode OR (positive AND (electrode OR active material OR pole material))) AND SFT=(lithium or lithium-ion or (lithium w5 ion) w5 (cell% or secondary batter* or batter* or accumulator)) AND STAC=(carbon or graphite) AND IPC=(C01B32* OR H01M4/133 OR H01M4/1393 OR H01M4/58*)
Si containing	STA=(anode OR (negative AND (electrode OR active material OR pole material))) NOT TI=(cathode OR (positive AND (electrode OR active material OR pole material))) AND SFT=(lithium or lithium-ion or (lithium w5 ion) w5 (cell% or secondary batter* or batter* or accumulator)) AND STAC=(Si OR silicon NOT SiO* NOT silica NOT silox* NOT *oxide) AND IPC=(C01B33/02* or H01M4/134 or H01M4/1395 or H01M4/38) AND IPC=(C01B33/02* or H01M4/134 or H01M4/1395 or H01M4/38)
SiO containing	STA=(anode OR (negative AND (electrode OR active material OR pole material))) NOT TI=(cathode OR (positive AND (electrode OR active material OR pole material))) AND SFT=(lithium or lithium-ion or (lithium w5 ion) w5 (cell% or secondary batter* or batter* or accumulator)) AND STAC=(SiO* OR silica OR silox* OR (silic* w3 *oxide)) AND IPC=(C01B33/113 or H01M4/131* or H01M4/1391* or H01M4/48*)
Sn containing	STA=(anode OR (negative AND (electrode OR active material OR pole material))) NOT TI=(cathode OR (positive AND (electrode OR active material OR pole material))) AND SFT=(lithium or lithium-ion or (lithium w5 ion) w5 (cell% or secondary batter* or batter* or accumulator)) AND STAC=(Sn or tin) AND IPC=(C01G19* or H01M4/131* or H01M4/134 or H01M4/1391* or H01M4/1395 or H01M4/38 or H01M4/48*)
Ti containing	STA=(anode OR (negative AND (electrode OR active material OR pole material))) NOT TI=(cathode OR (positive AND (electrode OR active material OR pole material))) AND SFT=(lithium or lithium-ion or (lithium w5 ion) w5 (cell% or secondary batter* or batter* or accumulator)) AND STAC=(Ti5O12 or titan*) AND IPC=(C01G23* or H01M4/131* or H01M4/1391*)

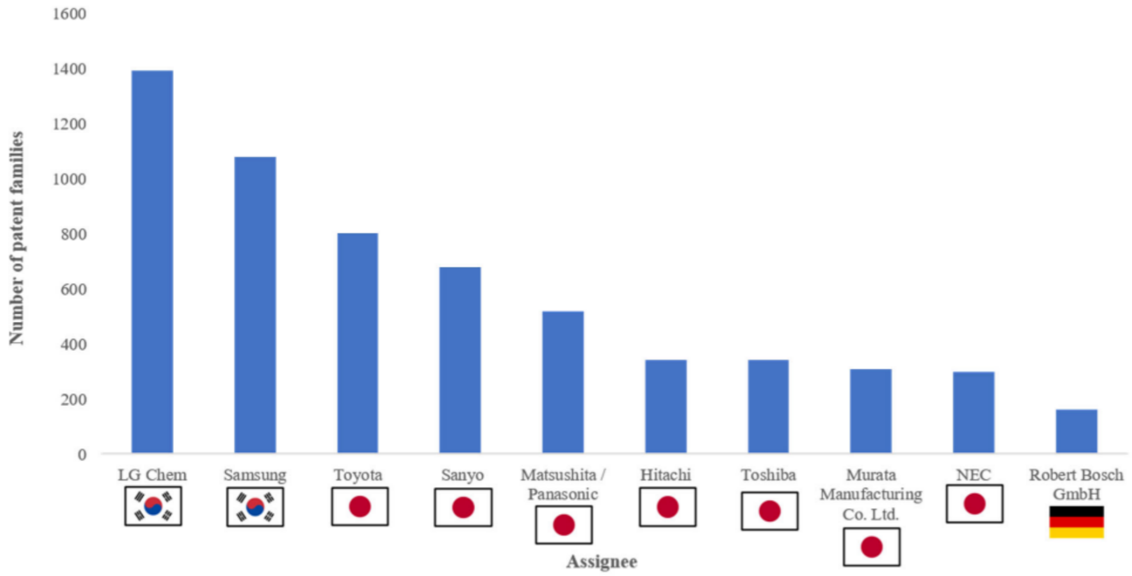
Appendix 2a. Most active assignees by country in phase 1 (1969-1991)



Appendix 3b. Most active assignees by country in phase 2 (1992-2009)



Appendix 4c. Most active assignees by country in phase 3 (2010-2018)



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