February 2020

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Connecting the dots in energy storage

Preview

Supercapacitors Innovation & Patent Review

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About the Author

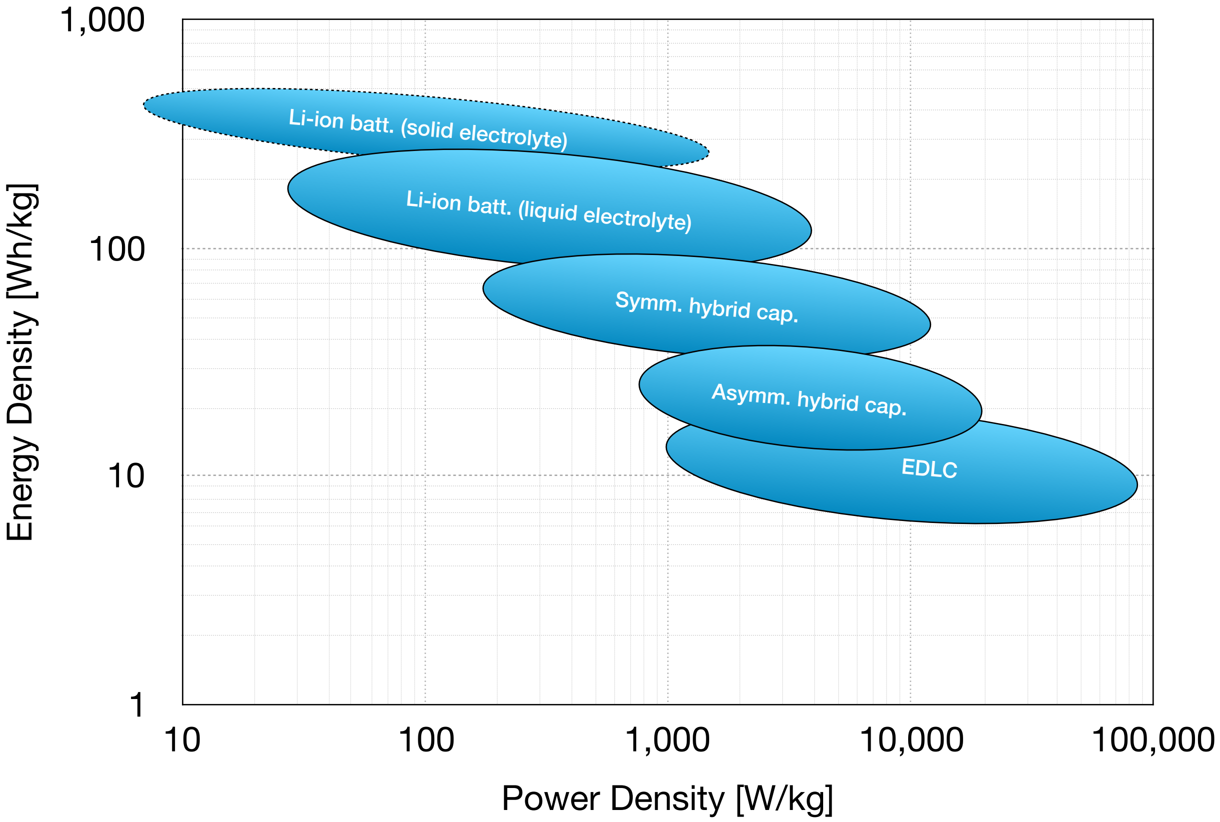
Pirmin Ulmann obtained a diploma in chemistry from ETH Zurich (Switzerland) in 2004 and a PhD from Northwestern University (USA) in 2009. Thereafter, he was a JSPS Foreign Fellow in an ERATO academic-industrial project at the University of Tokyo (Japan). From 2010 to 2016, while working at a major battery materials manufacturer in Switzerland, he was a co-inventor of 7 patent families related to lithium-ion batteries. He was also in charge of a collaboration with the Paul Scherrer Institute, evaluated outside technologies for corporate strategy, and made customer visits to battery manufacturers in East Asia, North America & Europe. He holds the credential Stanford Certified Project Manager (SCPM) and has co-authored scientific articles with more than 1,500 citations.

Introduction

How Do Supercapacitors Differ from Li-Ion Batteries?

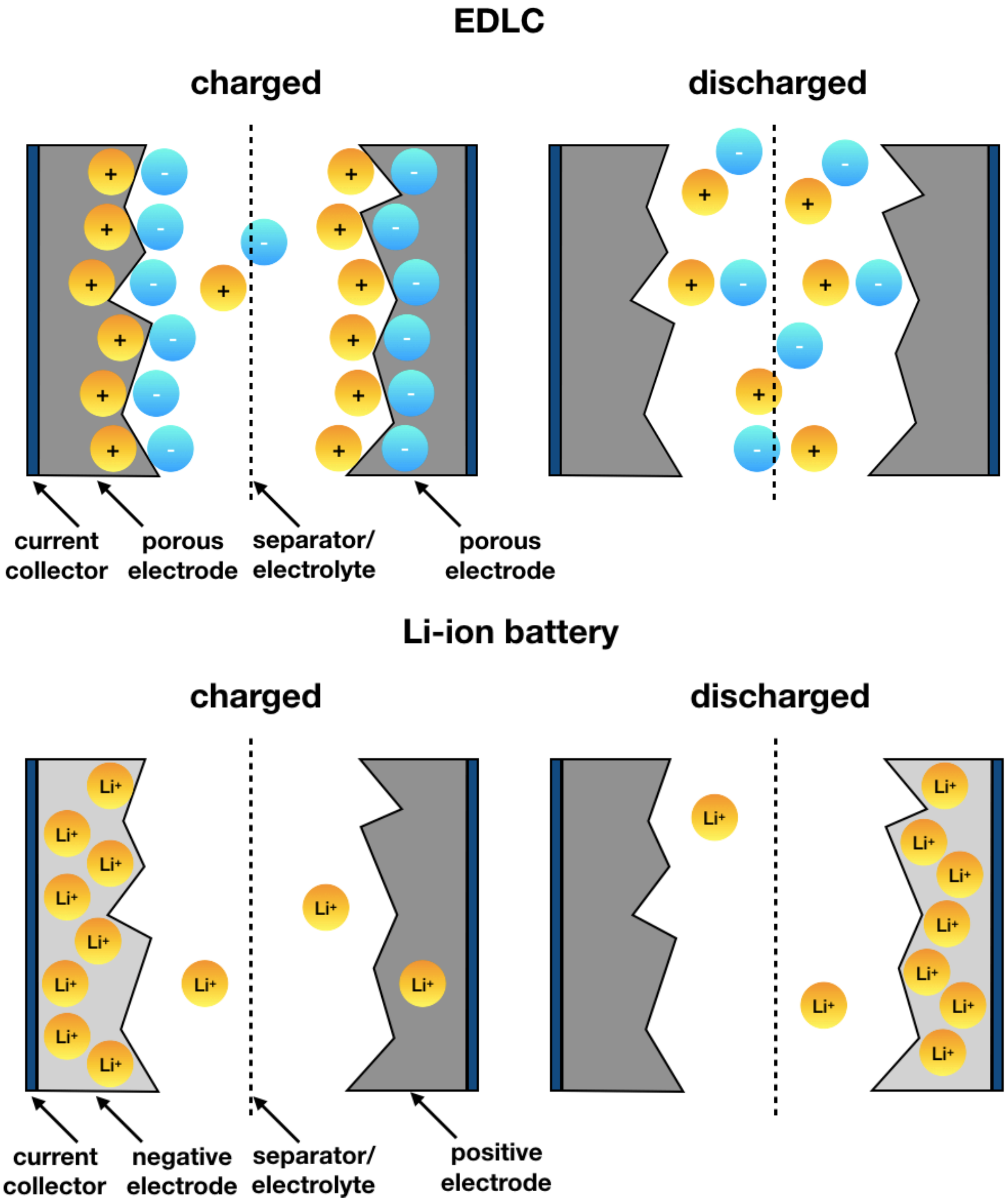
The three types of supercapacitors (Electrical Double Layer Capacitors = EDLCs, asymmetric and symmetric hybrid capacitors) differ from Li-ion batteries through superior power density while offering lower energy density (Figure 1).

Figure 1: Ragone diagram for different types of Li-ion batteries and supercapacitors, the oval for Li-ion batteries (solid electrolyte) represents automotive R&D targets by Toyota (stated at Battery Japan 2019), while the other ovals show approximate ranges of current technological feasibility.



These differences in power and energy density can be explained based on different charge storage mechanisms: 1) a fast electrostatic mechanism at the electrode-electrolyte interface for EDLCs (Figure 2, top), and 2) a slower electrochemical mechanism in which Li-ions move between electrodes for Li-ion batteries (Figure 2, bottom).

Figure 2: charged and discharged states in EDLCs (top) and Li-ion batteries (bottom)



Focus of this Review

This review is based on a machine learning-supported screening of newly published, commercially relevant supercapacitor patent families from across the globe (initial publication dates between January 1st, 2017 and October 15th, 2019).

While the patent screening was done for materials, cell & pack patents, in-depth technology stack analyses focus on materials aspects.

Terminology

Supercapacitors: for the purpose of this module, supercapacitors are defined as capacitors with high capacitance in which at least some part of charge storage occurs electrostatically (non-Faradaic/Helmholtz mechanism) rather than electrochemically (Faradaic mechanism).

EDLC: Electric Double Layer Capacitor. For the purpose of this module, the term EDLC is used for cells in which charge storage occurs by an electrostatic mechanism, usually based on carbon materials that do not intercalate significant amounts of lithium. The assumption has been made that metal oxides generally undergo electrochemical reactions in the patents studied and thus such electrodes are classified as hybrid capacitors rather than EDLC in this review.

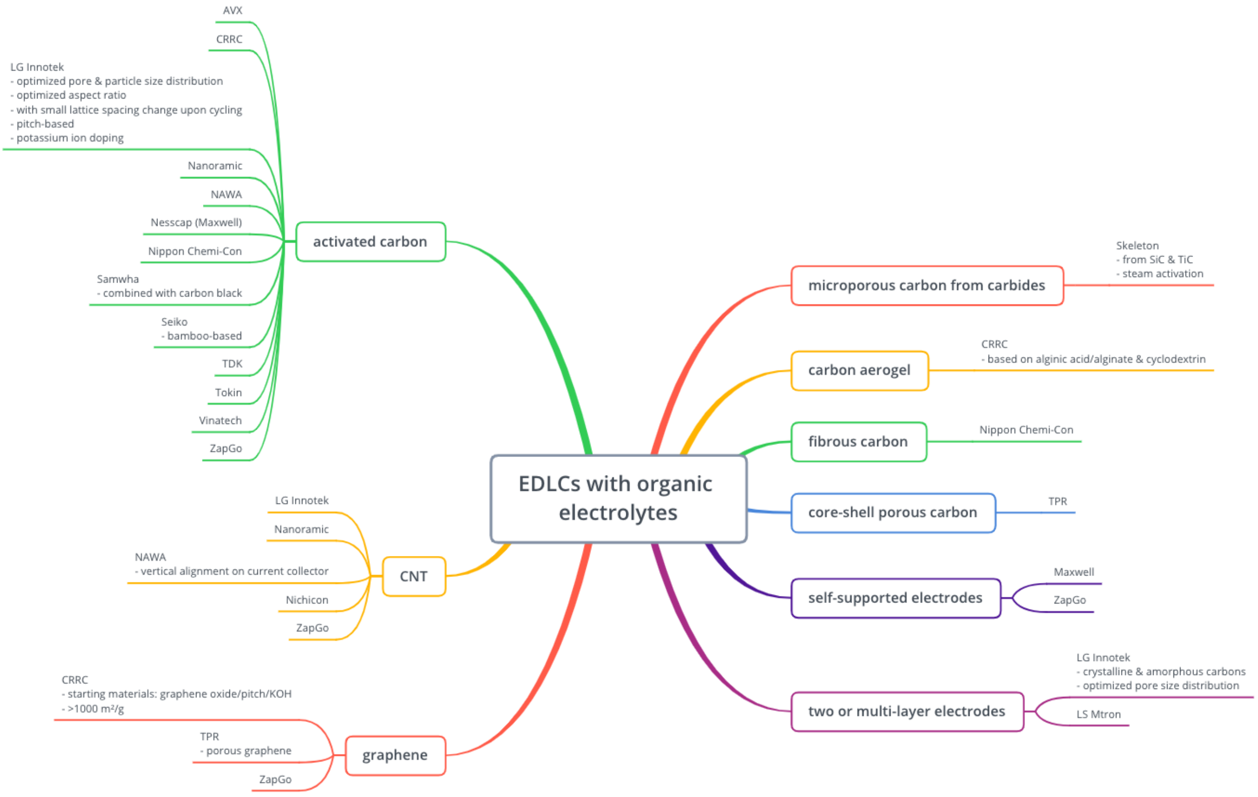
Asymmetric hybrid capacitors: contain one EDLC electrode that stores charge exclusively by an electrostatic mechanism and one mixed electrode with partial electrostatic and electrochemical energy storage. These capacitors generally have higher capacitances as compared to EDLCs at similar power performance, at the expense of increased manufacturing process complexity (handling of metallic lithium for pre-doping) and of reduced high temperature resistance (typical temperature limit: 70 °C, exceptions are mentioned below). The upper power density limit of asymmetric hybrid capacitor is 4-5 times lower as compared to EDLCs.

Symmetric hybrid capacitors: contain two mixed electrodes that each store charge electrostatically and electrochemically. They can be designed with higher capacitances than asymmetric hybrid capacitors at the expense of power performance, longevity, high temperature resistance, and inherent safety. Handling of metallic lithium/pre-doping can be avoided during manufacturing if lithium-containing metal oxides or the like are used as active materials.

Innovation Decision Tree for Supercapacitors

The innovation decision tree reflects how various organizations have made substantially different decisions as to what materials, concepts and engineering targets to focus on in their patenting activity. This decision tree should not be regarded as comprehensive, but hopefully as a source of inspiration for novel innovations. With few exceptions, only recent patenting activity is covered, not patents filed in earlier years that might already have covered a topic listed in the decision tree.

Figure 10: materials and electrode architectures for EDLCs with organic electrolytes



Activated carbons (Figure 10 above) remain much in focus of active material patenting activity for EDLCs (AVX, CRRC, LG Innotek, Nanoramic, NAWATechnologies, Nesscap/Maxwell, Nippon Chemi-Con, Samwha, Seiko Instruments, TDK, Tokin, Vinatech, ZapGo), while very important developments also occur with novel nanocarbons (used as major or minor electrode components), including CNTs (LG Innotek, Nanoramic, NAWATechnologies, Nichicon, ZapGo), graphenes (CRRC, TPR/TOC Capacitor, ZapGo), activated microporous carbons derived from carbides (Skeleton Technologies), carbon aerogels (CRRC), fibrous carbons (Nippon Chemi-Con), core-shell porous carbons (TPR). Although CNTs and graphenes have long been considered as very attractive active materials due to their high specific surface area, challenges relate to: 1) successful production of electrodes at large scale in which CNTs and graphenes are not aggregated into larger bundles that decrease the accessible surface area; 2) vertical alignment of anisotropic CNTs and graphenes in electrodes as not to block electrical and ionic conductivity.

With its ‘curved graphene’ active materials, Skeleton Technologies has been able to circumvent these problems, because ‘bundling’ is prevented and graphene nano-sheets are aligned to furnish relatively isotropic particles at the micrometer scale.

At the electrode architecture level, self-supported electrodes have been pursued that eliminate the need for a metal current collector foil (Maxwell, ZapGo), along with two or multi-layer electrodes that allow for advanced tuning of electrode properties at the cost of longer manufacturing procedures (LG Innotek, LS Mtron).

Machine Learning-Based Identification of Commercially Relevant Patents

b-science.net has developed a proprietary supervised machine learning methodology to assess the commercial relevance of patents, combined with an automatic translation framework that makes sure Non-English patents are identified. This methodology was validated as shown below. With this approach, we have comprehensively identified & classified patents by companies active in commercial R&D on supercapacitors.

In Table 1, the number of commercially relevant supercapacitor patent families newly published between 2017 and October 15th, 2019 are listed for 169 companies & company alliances.

For companies listed in bold, a technology stack analysis has been made. The selection has been made with a focus on novel high energy or high power supercapacitor materials.

Table 1: number of commercially relevant patent families (publication date of earliest patent family member between 2017 and October 15th, 2019)

Company	Country	2017	2018	2019 (until Oct 15th)	Total
[redacted]	[redacted]	31	28	37	**96**
[redacted]	[redacted]	21	36	12	**69**
[redacted]	[redacted]	14	11	31	**56**

Overview Material, Cell & Module Suppliers

Table 2: illustration of company positions along the supercapacitor supply chain, including links to product descriptions

Company Name	Active Materials	Separators	Electrolytes	Binders	Current Collectors	Cells/ Modules
[redacted]						Product Description
[redacted]						Product Description Cells, Modules, Systems
[redacted]						Product Description
Total	**13**	**2**	**3**	**2**	**5**	**47**

Classification According to Capacitor Type

Table 3: assignment of technology stacks to capacitor types (EDLCs, asymmetric, symmetric hybrid capacitors), major technology stacks are indicated in dark blue, minor stacks in light blue

Company Name	EDLC	Asymmetric Hybrid Capacitors	Symmetric Hybrid Capacitors
[redacted]	■		
	■		
	■		
	■ discontinued		
Total remaining (discontinued/ phasing out)	**24 (2)**	**16**	**11**

Classification According to Application Focus

Table 4: assignment of companies to end applications (electronics - semiconductors & IT, electronics - power tools and the like, automotive/rolling stock, stationary)

Company Name	Electronics - Semiconductors & IT	Electronics - Power Tools and the Like	Automotive/ Rolling Stock	Stationary
[redacted]	■			
	■ discontinued			
	■			
	■			
Total remaining (discontinued/ phasing out)	**15 (2)**	**17**	**22**	**17**

Technology Stacks by Key Companies

Patent families listed below with initial publication dates after 2018-07-17 (cut-off date 1st edition of this review) are labelled orange: e.g. #1. Patent families with initial publication dates between 2017-01-01 and 2018-07-17 are displayed in black: e.g. #1.

Nippon Chemi-Con - Japan

Organization profile

Nippon Chemi-Con Corp. (http://www.chemi-con.co.jp/e/index.html, FT profile, product description) is a manufacturer of various kinds of capacitors, including supercapacitors, aluminum electrolytic capacitors, multilayer ceramic capacitors, film capacitors. In the US, the company operates as United Chemi-Con.

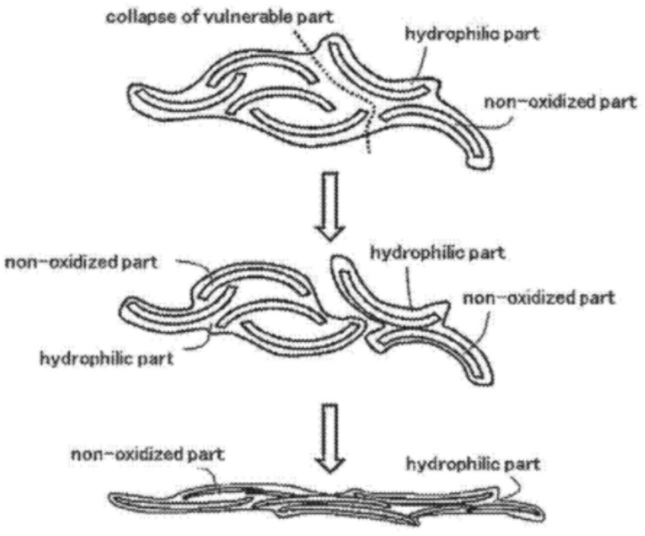
What's New?

The DLCAP DXF series cylindrical EDLC was newly introduced into the product portfolio (3,500 F, ca. 4.3 Wh/kg energy density, can be used at 3.0 V, -40°C to +50°C).

Patenting activity suggests that Nippon Chemi-Con intends to push towards higher energy density through the replacement of LTO with tailored Li_3VO_4-based crystalline materials, which at the same time offer favorable power capability.

Furthermore, a novel type of conductive carbon additive has been developed in which inaccessible void space has been reduced (see Figure 20 below). These conductive carbon additives probably correspond to NH Carbon additives that were promoted by Nippon Chemi-Con with a leaflet at Battery Japan 2019 for Li-ion batteries (close alignment of carbon black with active material leads to improved cycle life and Coulombic efficiency, press report).

Figure 20: conductive carbon in which inaccessible void space has been reduced (Nippon Chemi-Con)



General comments on patent portfolio

Technology stack 1 provides a toolbox of high performance materials, processes, cell and module architectures for all supercapacitor types, and in many cases also for aluminum electrolytic capacitors.

The main focus of EDLC technology stack 2 lies on wide temperature performance (-40 to 85 °C) with γ-butyrolactone electrolytes through the use of activated carbons supported by fibers.

Targets of asymmetric hybrid capacitor technology stack 3 are: 1) increased energy density through the introduction of Li_3VO_4, and 2) increased reliability of LTO-based capacitors through the avoidance of gas formation.

In summary, Nippon Chemi-Con has a versatile toolbox at its disposal to build many types of high performance capacitors, with small scales used in electronics applications to larger scales used in automotive and stationary applications.

Technology stack 1 - generally applicable materials and processes

Conductive additives: conductive carbon with unique pore structure based on acid treated Ketjen black (EC300J, ca. 800 m^2/g BET SSA), acetylene black, and sacrificial LFP, which serves as compression agent that is later removed (#1, #2, #3, #4).

Cells: with 2-layer sealing architecture that balances sealing, rigidity and gas pressure adjustment (#1), with a pseudo-cathode foil for over-voltage protection (#2). Optimized winding/molding processes for high capacitance electrodes (#3, #4, #5).

Modules: architecture for improved impact resistance, vibration resistance, and heat dissipation characteristics (#1).

Technology stack 2 - EDLC cells with high temperature resistance and reliability

Electrodes: based on fibrous carbons and activated carbons (#1, #2), fibrous celluloses and activated carbons (#3), in which the electrode active material layer is divided into a plurality of small regions by a dividing portion (#4).

Cells: based on γ-butyrolactone electrolytes, with low internal resistance (#1).

Technology stack 3 - asymmetric hybrid capacitors based on LTO or Li_3VO_4

Active materials: Li_3VO_4-based crystalline material with higher capacity as compared to LTO (#1), LTO in which the gas generation inhibitor Na_2TiO_3 is incorporated (#2).

Cells: with Li-absorbing metal oxide (e.g. LTO) or metal-based anodes and activated carbon in fibrous carbon cathodes (#1), with low resistance (#2).

Patent Analysis Methodology & Validation

The patent information source for this review is the European Patent Office (EPO), which covers patent filings from more than 100 patent offices around the world. >1.8 Mio. patent documents are included in the b-science.net database that were published since 1980, which either contain the words 'battery' or 'batteries' in the title or abstract, or were assigned to one of the energy storage-related CPC (cooperative patent classification) or IPC (international patent classification) codes: H01M (batteries & fuel cells) or H01G (capacitors). In this review, patent families published between January 1st, 2017 and October 15th, 2019 (publication date of earliest family member) were screened. Patent families that were not available in English in the EPO database were Google machine translated (titles, abstracts, applicants). Some Google translations of applicants were manually corrected. A machine learning (ML) model was defined for commercially relevant supercapacitor patents. Patent documents were grouped into patent families and scored with the ML models. An ML relevancy score cutoff value of 70 was applied (100: very relevant, 0: not relevant).

The **methodology was validated** with patent families filed by LS Mtron. 40 patent families by LS Mtron were manually classified as relevant. All of these patent families exhibit an ML score of >70 (higher than cutoff value). 27 patent families by LS Mtron were manually classified as not relevant and exhibit an ML score of <70 (lower than cutoff value).

List of Abbreviations

BET	Brunauer–Emmett–Teller (theory used to determine surface area through gas adsorption measurement)
BMIM	1-Butyl-3-methylpyrrolidinium (ionic liquid cation, sometimes abbreviated as BMI)
CMC	Carboxymethyl Cellulose (binder)
CNF	Carbon Nanofibers (conductive additive or active material)
CNT	Carbon Nanotubes (conductive additive or active material)
CVD	Chemical Vapor Deposition
DMC	Dimethyl Carbonate (electrolyte component)
EC	Ethylene Carbonate (electrolyte component)
EDLC	Electrical Double Layer Capacitor
EMC	Ethyl Methyl Carbonate (electrolyte component)
EMIM	1-Ethyl-3-methylimidazolium (ionic liquid cation, sometimes abbreviated as EMI)
EPS	Electric Power Steering
ES	Ethylene Sulfite (electrolyte additive)
ESR	Equivalent Series Resistance
HMDS	Hexamethyldisiloxane (electrolyte additive)
EV	Electric Vehicle
FT	Financial Times
IoT	Internet of Things
KAIST	Korea Advanced Institute of Science and Technology
LCO	Lithium Cobalt Oxide, $LiCoO_2$ (Li-ion battery cathode material)
LFP	Lithium Iron Phosphate, $LiFePO_4$ (Li-ion battery cathode material)
LiFSI	Lithium bis(fluorosulfonylimide) (electrolyte salt)
LMO	Lithium Manganese Oxide, $LiMn_2O_4$ (Li-ion battery cathode material)
LNMO	Lithium Nickel Manganese Spinel, $LiNi_{0.5}Mn_{1.5}O_4$ (Li-ion battery cathode material)

LTO	Lithium Titanium Oxide, Li_2TiO_3 (Li-ion battery anode material)
MCF	Mesophase Pitch Carbon Fibers (conductive additive or active material)
MCMB	Mesocarbon Microbeads (Li-ion battery anode material)
NMC	Lithium Nickel Cobalt Manganese Oxide, $LiNiCoMnO_2$ (Li-ion battery cathode material)
NCA	Lithium Nickel Cobalt Aluminum Oxide, $LiNiCoAlO_2$ (Li-ion battery cathode material)
PAA	Polyacrylic Acid (polymer)
PC	Propylene Carbonate (electrolyte)
PCB	Printed Circuit Board
PE	Polyethylene (polymer)
PEG	Polyethylene Glycol (polymer)
PP	Polypropylene (polymer)
PTFE	Polytetrafluoroethylene (binder)
PVA	Polyvinyl Alcohol (polymer)
PVC	Polyvinyl Chloride (polymer)
PVDF	Polyvinylidene Difluoride (binder)
SBR	Styrene-Butadiene Rubber (binder)
SEI	Solid Electrolyte Interphase (intermediate layer between electrode and electrolyte)
SSD	Solid-State Drive (information storage device)
SEM	Scanning Electron Microscopy
SMD	Surface-Mount Device
SOC	State-Of-Charge (between 0 and 100%)
SSA	Specific Surface Area (usually determined using a BET measurement)
SWCNT	Single-Wall Carbon Nanotubes (conductive additive or active material)
TEA	Tetraethylammonium (non-coordinating cation)
TFSI	Bis(trifluoromethane)sulfonimide (non-coordinating anion)
UPS	Uninterruptible Power Source (end application)
VC	Vinylene Carbonate (electrolyte additive)
VGCF	Vapor Grown Carbon Fibers (conductive additive or active material)

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