

SLW Life Sciences Webinar Series

What We Can Learn about Technology Landscapes from Patent Citation Analyses— CASE STUDY OF LITHIUM ION BATTERY PATENTS

February 11, 2025



Before We Get Started...

Recording

Questions



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Panel



Janal Kalis, J.D. Patent Attorney & Principal Nicholas Lanzatella, J.D., Ph.D. Patent Attorney & Principal



Definitions

- **Backward citations** are patents that are cited in a patent and that were considered by a USPTO examiner in prosecuting a patent application. Cites are on the face of the patent.
- Forward citations are patents citing an issued patent or published patent application. Can be found in databases like Derwent
- USPTO database is preferable to use because of penalties for not citing material prior art.



Red Flags Identified by Ratio of Forward: Backward Citations

- Backward Citations: Always check claims to make sure product being commercialized does not infringe claims in these patents;
- Backward Citations >> Forward Citations: Check owners and patent status, Check claims— Most Inventions Are Incremental Improvement
- Backward Citations about=Forward Citations—Invention is incremental improvement
- Forward Citations>>Backward Citations—Invention may be a blockbuster





Options for Studying Citations

Map by patent owners

Map by inventors

Map by independent claims



The Story Starts in the Exxon Lab of M. Stanley Whittingham in the Early 1970s



https://www.nobelprize.org/prizes/chemistry/2019/whittingha m/facts/



Whittingham developed a battery with a titanium-disulfide cathode and a liquid electrolyte that used lithium ions.







Whittingham's Battery

Whittingham's battery was new and unobvious. It worked by inserting ions into an atomic lattice of a host electrode material. The battery was both rechargeable and very high in energy output.

Before the Whittingham battery, the best rechargeable battery had been nickel cadmium, which put out a maximum of 1.3 volts.

Whittingham's battery produced 2.4 volts.



Exxon Invested in the Battery



 Exxon began manufacturing coin cell lithium batteries, and a Swiss watch manufacturer, <u>Ebauches</u>, used the cells in a solar-charging wristwatch.



Exxon Filed a Patent Application: US4009052

[54] CHALCOGENIDE BATTERY

- [75] Inventor: M. Stanley Whittingham, Fanwood, N.J.
- [73] Assignee: Exxon Research and Engineering Company, Linden, N.J.
- [22] Filed: Apr. 5, 1976
- [21] Appl. No.: 673,696

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 552,599, Feb. 24, 1975, abandoned, which is a continuation-in-part of Ser. No. 396,051, Sept. 10, 1973, abandoned.



Exxon Filed a Patent Application: US4009052

What is claimed is:

1. A battery comprising:

- a. an anode containing as the anode-active material a metal selected from the group consisting of Group *la* metals, Group *lb* metals, Group *Ila* metals, Group *Ilb* metals, Group *IIIa* metals, Group *IVa* metals, and mixtures containing the aforesaid metals such that the aforesaid metals can be electrochemically released from the mixtures;
- b. a cathode with a sole cathode-active material consisting essentially of
 - 1. a layered chalcogenide of the formula MZ_x wherein M is an element selected from the group consisting of titanium, zirconium, hafnium, niobium, tantalum and vanadium; Z is an element selected from the group consisting of sulfur, selenium and tellurium, and x is a numerical value between about 1.8 and about 2.05 or (2) alloys of the aforesaid chalcogenides with one another, said chalcogenides having a structure which will permit intercalation therein by ions of the anodeactive material; and
- c. an electrolyte which does not chemically react with said anode or said cathode and which will permit the migration of ions from said anode-active material to intercalate said cathode-active material.



Forward and Backward Citation of Pioneer Patent US4009052

- 3 Backward Citations
 - Bell Telephone (2X)
 - Mallory & Co—A Battery Co.
- 157 Forward Citations
 - Duracell-8—Mallory Co—Dry Cell (alkaline, Mercury)
 - Medtronic-23-In 1975, some Medtronic pacemakers with Mercury batteries shorted out
 - Exxon-13
 - No JP companies





Forward and Backward Citation

Medtronic eventually developed its own Lithium battery.

- In 1970 Medtronic implanted a nuclear powered pacemaker.
- The nuclear battery in the Medtronic device used a tiny 2.5 Ci slug of metallic Plutonium 238 (Pu-238). The radiation produced by the Pu-238 bombarded the walls of its container, producing heat that a thermopile then converted to an electrical current.



Nuclear Powered Pacemaker Developed by Medtronic and Alcatel





Exxon Got Out of the Business of Making Batteries

- In the early 1970s, Exxon scientists predicted that global oil production would peak in the year 2000 and then fall into a steady decline.
- By the late 1970s, Exxon's interest in oil alternatives had waned and Exxon thought Whittingham's concept was unlikely to ever be broadly successful. They washed their hands of lithium titanium disulfide.
- The technology languished for the next 15 years.



The Handoff to John Goodenough and Koichi Mizushima at Oxford University



https://www.facebook.com/JapanPrizeAward/posts/in-1980-lithium-ion-battery-development-made-a-leap-forward-with-the-demonstrati/570722873289434/



Goodenough and Mizushima

In 1980, Goodenough and Mizushima improved on Whittingham's design, replacing titanium disulfide with lithium cobalt oxide. The new chemistry boosted the battery's voltage by another two-thirds, to 4 volts.

4 4



Goodenough and Mizushima Battery



Obtained from https://spectrum.ieee.org/lithium-ion-battery-2662487214



Patenting Goodenough Battery

- Goodenough asked the University of Oxford to pay for a patent, but Oxford declined. Oxford's
 position was that it did not concern itself with IP, believing such matters to be confined to the
 commercial world.
- Goodenough visited the <u>Atomic Energy Research Establishment</u> (AERE), a government lab in Harwell, UK, about 20 kilometers from Oxford. The lab agreed to bankroll the patent, but only if Goodenough signed away his rights. Goodenough complied. The lab patented the Goodenough battery in 1981; Goodenough never saw a penny of the original battery's licensing earnings.

AERE filed the patent away and forgot about it—until they were contacted by Sony, 8 years later.



Two Patents for AERE: US4302518

United	States	Patent	[19]
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Goodenough et al.

- [54] ELECTROCHEMICAL CELL WITH NEW FAST ION CONDUCTORS
- [76] Inventors: John B. Goodenough; Koichi Mizuchima, both of c/o United Kingdom Atomic Energy Authority, 11 Charles II St., London SW1Y 4QP, England
- [21] Appl. No.: 135,222
- [22] Filed: Mar. 31, 1980
- [30] Foreign Application Priority Data
 - Apr. 5, 1979 [GB] United Kingdom 11953/79



Goodenough et al. Patent Claim: US4302518

The '518 patent protected crystalline compounds which promote fast alkali metal-ion transport, including those with the formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ where 0 < x < 3. These materials would come to be termed "NASICONs" – an acronym for sodium (Na) Super Ionic CONductor.

1. An ion conductor, of the formula $A_x M_y O_2$ and having the layers of the α -NaCrO₂ structure, in which formula A is Li, Na or K; M is a transition metal; x is less than 1 and y is approximately equal to 1, the A⁺ cation vacancies in the ion conductor having been created by A⁺ cation extraction.



Forward and Backward Citations for '518

- 3 Backward Citations
 - Dupont
 - GE
 - Bell



- 167 Forward Citations
 - Matsushita-11—Makes batteries
 - Semiconductor Energy—35—Makes Transistors + Semiconductors
 - 0 for Medtronic



Next Generation Citation Map for '518





US4357215

United States Patent [19]

Goodenough et al.

[54] FAST ION CONDUCTORS

- [76] Inventors: John B. Goodenough; Koichi Mizushima, both of United Kingdom Atomic Energy Authority, 11 Charles II St., London SW1Y 4QP, England
- [21] Appl. No.: 259,104
- [22] Filed: Apr. 30, 1981

Related U.S. Application Data

- [62] Division of Ser. No. 135,222, Mar. 31, 1980, Pat. No. 4,302,518.
- [30] Foreign Application Priority Data
 - Apr. 5, 1979 [GB] United Kingdom 7911953



US4357215

1. A method of making an ion conductor of the formula $A_x M_y O_2$ and having the layers of the α -NaCrO₂ structure, in which formula A is Li, Na or K, wherein M is a transition metal, wherein x is less than 1; and wherein y is approximately equal to 1 which method comprises extracting A⁺ cations from a compound having the formula $A_{x'}M_yO_2$ wherein A, M, and y are as defined hereinbefore and wherein x' is less than or equal to 1.



Forward and Backward Citations

- Backward-3
- Forward-53
 - Samsung-10
 - Matsushita-5
 - Medtronic, Motorola, Asahi, MIT





More on Goodenough Patents

Goodenough et al. obtained a patent for a new cathode material. <u>European Patent No. 0 017</u> <u>400</u> was granted in 1984, with siblings granted in Japan and the US. The patents were owned by United Kingdom Atomic Energy Authority, whose site in neighboring Harwell had provided funding to the Oxford team. The patent application filing date was in 1980. However, commercialization of Lithium Ion Batteries took about another 10 years with the invention of graphite anodes.



Next Up: Akira Yoshino and Asahi Glass



https://www.wipo.int/web/wipo-magazine/articles/the-invention-of-rechargeable-batteries-an-interview-with-dr-akira-yoshino-2019-nobel-laureate-41566



Yoshino Develops Safer Lithium Battery

Yoshino had independently begun to investigate using a plastic anode—made from electroconductive polyacetylene—in a battery and was looking for a cathode to pair with it. Yoshino paired Goodenough's cathode with a plastic anode—a carbon-based anode made from petroleum coke.



Yoshino Developed Safer Lithium Battery



Obtained from https://spectrum.ieee.org/lithium-ion-battery-2662487214



Yoshino Develops Safer Lithium Battery

- This choice of petroleum coke turned out to be a major step forward. Whittingham and Goodenough had used anodes made from metallic lithium, which was volatile and even dangerous. By switching to carbon, Yoshino and his colleagues had created a battery that was far safer.
- Still, there were problems. For one, Asahi Chemical was a chemical company, not a battery
 maker. No one at Asahi Chemical knew how to build production batteries at commercial
 scale, nor did the company own the coating or winding equipment needed to manufacture
 batteries. The researchers had built a crude lab prototype.



Yoshino Patent: US4668595

Yoshino et al.			
[54]	SECONDARY BATTERY		
[75]	Inventors:	Akira Yoshino, Fujisawa; Kenichi Sanechika; Takayuki Nakajima, both of Kawasaki, all of Japan	
[73]	Assignee:	Asahi Kasei Kogyo Kabushiki Kaisha, Osaka, Japan	
[21]	Appl. No.:	861,423	
[22]	Filed:	May 9, 1986	
[30] Foreign Application Priority Data			
Ma Ma Jur Jur Jur	y 10, 1985 [J] y 11, 1985 [J] y 11, 1985 [J] n. 18, 1985 [J] n. 18, 1985 [J] n. 18, 1985 [J]	P] Japan	
[51] [52] [58]	Int. Cl. ⁴ U.S. Cl Field of Sea 42	H01M 10/40 429/194; 429/218 arch	

United States Patent [19]



Yoshino Patent Claim 1

 A secondary battery comprising positive and negative electrodes, a separator, and a nonaqueous electrolyte, wherein said secondary battery is characterized by having as an active material for either of said positive and negative electrodes:

I: a composite oxide possessing a layer structure and represented by the general formula:

A_xM_yN_zO₂

wherein A is at least one member selected from the group consisting of alkali metals, M is a transition metal, N is at least one member selected from the group consisting of Al, In, and Sn, and x, y, and z satisfy the expression, $0.05 \le x \le 1.10$, $0.85 \le y \le 1.00$, and $0.001 \le z \le 0.10$, respectively, and

II: an n-doped carbonaceous material which has a BET-method specific surface area, A (m²/g), being in the range of 0.2 < A < 100 and a crystal thickness, Lc (Å), based on X-ray diffraction and a true density, ρ (g/cm³), which satisfies the conditions, $1.70 < \rho < 2.18$ and $10 < Lc < 120\rho - 189$.



Forward and Backward Citations

- Backward Citations—3—All Goodenough patents
- Forward Citations—288





Asahi Forward/Backward Citations



- 3/288--Backward/Forward
- Backward cites are 3 Goodenough patents
- Semiconductor Energy Lab cited Asahi '595 patent in 35 of its patents
- Sony cited '595 patent in 3 of its patents
- Medtronic cited '595 patent in 9 of its patents



Citation Map for '595 Patent





Making a Better Prototype: Battery Eng and Nikola Marincic

- No one at Asahi Chemical knew how to build production batteries at commercial scale, nor did the company own the coating or winding equipment needed to manufacture batteries.
- Asahi Chemical hired Battery Engineering, a small firm based in a converted truck garage in the Hyde Park area of Boston. The company was run by a small group of PhD scientists who were experts in the construction of unusual batteries.
- Kuribayashi of Asahi flew to Boston in June of 1986, showing up at Battery Engineering unannounced with three jars of slurry—one containing the cathode, one the anode, and the third the electrolyte. They asked company cofounder <u>Nikola Marincic</u> to turn the slurries into cylindrical cells, like the kind someone might buy for a flashlight.





Nikola Marincic





Making the Prototype

- Marincic charged \$30,000 (\$83,000 in today's dollars) to build a batch of the batteries. Two weeks later, Kuribayashi and his colleague departed for Japan with a box of 200 C-size cells.
- Kuribayashi said to Marincic: "If you want to build the batteries, then don't ask any more questions,"
- Kuribayashi and his colleague further stipulated that Marincic tell no one about their battery. Even Marincic's employees didn't know until 2020 that they had participated in the construction of the world's first preproduction lithium-ion cells.
- Marincic obtained a patent on a Lithium Ion Battery with carbon-based cathodes that issued in 1996—US5514492 (93 forward/11 backward)



On the Road to Commercialization

- Kuribayashi showed the prototype batteries to engineers in Sony's camcorder division in 1987. The Sony engineers saw the value of the prototype batteries.
- Yoshio Nishi's team at Sony developed binders, electrolytes, separators and additives for making a commercial battery. One patent from this group is US4959281.



Citation Chart for Sony US4959281 Patent

- Backward Citations--6:
 - Sharp-2X
 - Asahi-1
 - Sanyo-1
 - Mitsubishi-2X
- Forward Citations--97:
 - Univ. Texas-6
 - Gillette—12
 - Hydro Quebec-7





Sony-AERE Licensing Agreement

- In 1989, about 8 years after issuance, Sony called the AERE and asked about Goodenough's cathode patents. Sony was interested in obtaining a license. Executives at AERE did not understand why Sony was interested but did grant of license to Sony.
- Sony introduced the battery in 1991 in camcorders, then cellphones.
- AERE reaped \$50M to perhaps over \$100M in royalties.





No \$\$\$ But Nobel Prizes

None of the original investigators—Whittingham, Goodenough and Yoshino received a cut of the profits. All three shared the 2019 Nobel Prize in Chemistry.



Nobel Prize Winners



John B Goodenough, M Stanley Whittingham and Akira Yoshino are the Nobel laureates in chemistry for 2019 Photograph: Niklas Elmehed/Royal Swedish Academy of Sciences

https://www.theguardian.com/science/2019/oct/09/nobel-prize-in-chemistry-awarded-for-work-on-lithium-ion-batteries



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Thank you for your interest.

Questions?



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