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Invention Article

Fluorination of lithium metal used as anode in lithium metal batteries

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ABSTRACT

This invention refers to an innovative treatment capable of forming a coating on metallic lithium. This coating is able to solve the problem of dendritic growth, which represents a safety risk for batteries in terms of overheating or even catching fire. It is a process for the surface fluorination of metallic lithium using elemental fluorine. In this way, a uniform and impurity-free surface layer of lithium fluoride is formed on the whole surface of metallic lithium. This highly reproducible treatment can also be carried out on a large scale; it allows the creation of a material that can be advantageously used as anode in lithium batteries, since it guarantees significantly higher performances than those obtained by using bare metallic lithium anodes, and also those with lithium metal anodes equipped with a lithium fluoride layer, in which the creation of a lithium fluoride layer is achieved in situ by organic or other inorganic fluorinating agents.

1. Specifications table

xxxxx

Subject code	*2505 Materials Chemistry*
Specific subject area	*Process for the surface fluorination of metallic lithium using elemental fluorine*
Industry code	*H01M 4/134 (Electrodes based on metals)* *H01M 4/38 (Electrodes based on elements or alloys)* *H01M 4/1395 (Process of Manufacture of Electrodes based on metals)* *H01M 10/00 (Secondary cells; Manufacture thereof)* *C23C 8/08 (Chemical surface treatment of metallic material)*
Details of inventors	Maurizio Sansotera (Politecnico di Milano – maurizio.sansotera@polimi.it) Luca Magagnin (Politecnico di Milano – luca.magagnin@polimi.it) Eugenio Gibertini (Politecnico di Milano – eugenio.gibertini@polimi.it) Piergiorgio Marziani (Politecnico di Milano – piergiorgio.marziani@polimi.it) Walter Navarrini (walter.navarrini@polimi.it)
Dates of invention	*Conception of the invention: November 2019* *The international patent application was published on July 21st, 2022 (international publication number: WO 2022/153,169 A1)*
Patent details *(Only if patented)*	*The priority patent application was filed on January 15th, 2021 (application number 102,021,000,000,704); an international patent application was filed on January 11th, 2022 (international application number: PCT/IB2022/050,172). National phases have been filed in Europe, China, South Korea, Australia, Canada, and the USA.* *The Italian Patent has been published on January 24th, 2023. Both the application and the publication have the reference number* 102,021,000,000,704. *Patent owner: Politecnico di Milano* *Patent attorney or agent: Perani & Partners (Raffaella Asensio)* *Contact for service: Massimo Barbieri (Politecnico di Milano, Technology Transfer Office)* *Link to the international patent application:* https://worldwide.espacenet.com/patent/search/family/074875247/publication/WO2022153169A1?q=pn%3DWO2022153169A1
Intended use	*The invention is exclusively available for licensing to the spin-off start-up "LIFT Energy s.r.l."*

(continued on next page)

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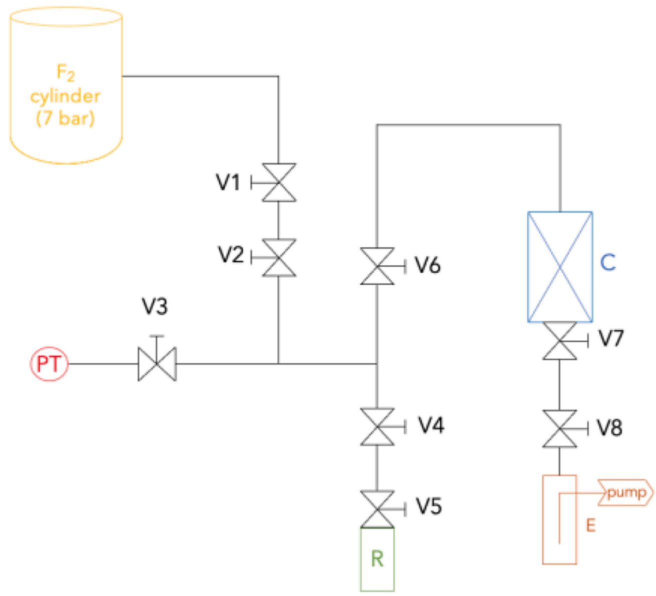

Fig. 1. Steel vacuum line scheme. R: fluorination reactor. C: soda lime scrubber. E: liquid nitrogen cold trap. PT: pressure gauge.

(*continued*)

	interested in the implementation of this technology in the field of energy storages.
Related research article	*N/A*
Related other sources: (datasets, software, diagrams, plans, etc.)	*N/A*

2. Value of the invention

- The treatment object of this invention forms a stable and safe coating on metallic lithium.
- The treatment object of this invention solves the problem of the dendritic growth on metallic lithium.
- The overall process described in this invention is highly reproducible and scalable.
- The treatment can be used by lithium battery manufacturers for the production of stable anodes of metallic lithium.
- Anodes of metallic lithium stabilized by the treatment guarantee much higher performances in the final assembly of the batteries, in terms of energy density and safety.

3. Invention description

3.1. Fluorination line

The fluorination line is a batch stainless-steel laboratory-scale plant used to synthesize, purify, and polymerize fluorinated compounds. The fluorination reactions on metallic lithium anodes were performed with elemental fluorine, F_2, by using a stainless-steel reactor connected to the stainless-steel vacuum line of the fluorination laboratory-scale plant. This part of the fluorination plant was equipped with a pressure gauge, that allowed the regulation of the pressure of elemental fluorine during the treatments. The stainless-steel vacuum line was also equipped with a diffusive pump connected in sequence to a rotative pump, in order to vent the reactor at the end of the reactions. A safety cold trap cooled with liquid nitrogen is connected to the vacuum line before the suction connection of the pumps and, between the cold trap and reactor, a soda lime scrubber heated at 200 °C was present for the abatement of exhaust gases. Connections for nitrogen, N_2, and argon, Ar, were also present because these gases were used for purging the reactor. Elemental fluorine with a purity of 98 % was stored in a cylinder at 7 bars located in a safety cabinet which allows F_2 safe storage and handling: the cylinder can be opened and closed by a manual actuator that avoid contact between the operator and the cylinder; F_2 pressure is regulated by a remotely controlled pressure reducer and is monitored by two pressure gauges after the cylinder. The scheme of the stainless-steel vacuum line is reported in Fig. 1.

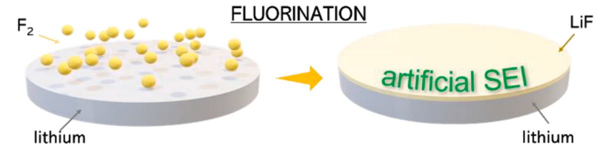

Fig. 2. Formation of the artificial SEI on the lithium surface.

3.2. Formation of the artificial SEI

During battery cyclings, metallic lithium reacts with the electrolyte and a passivation layer forms on its surface. This layer, called Solid Electrolyte Interphase (SEI), is generated by electrochemical decomposition of the electrolyte at potential lower than 1.5 ÷ 1.2 V vs Li^+/Li. The typical SEI is ionically inhomogeneous and in combination with lithium plating, forms many dendrites. These huge dendrites can get through the separator causing short circuits and overheating effects with thermal runaways and explosions. The fluorination of lithium produces a superficial layer of inorganic lithium fluoride, that behaves as a compact and artificial SEI (Fig. 2).

The SEM image of a fluorinated lithium disk (Fig. 3) confirmed the formation of a thick layer on Li metal surface: this layer is ascribable to LiF synthesis due to direct lithium fluorination. Before SEM analysis, the disk was also mechanically bended in order to observe its cross section: thus, a LiF thickness of approximately 1.25–2.5 μm was measured.

XRD analysis (Fig. 4) confirmed the formation of a crystalline LiF phase. In particular, no by-products formation was detected.

3.3. Electrochemical measurements

Symmetric Li-Li and LiF-LiF cells were assembled for the evaluation of the electrochemical performances. Plating and stripping tests, with a current density of 1 mA cm^{-2} and a lithium capacity of 1 mAh cm^{-2}, have been performed on both cells. During battery charging, lithium plating reaction creates a metallic lithium phase that progressively accumulates on anode surface (Eq. (1)):

$$Li^{+}_{electrolyte} + e - \rightarrow Li_{plated} \tag{1}$$

This deposition process takes place at the anode in lithium metal batteries, instead of lithium-ion intercalation typical of lithium-ion batteries. In the presence of bare metallic lithium, several degradation processes occurring at the interface induce the formation of the solid-electrolyte interphase (SEI) which stabilizes the battery but accelerates the loss of part of the active lithium. The beneficial effect of the LiF coating is reported in Fig. 5. The Li/Li symmetrical cell clearly showed an increase of cell internal impedance by multiple plating/stripping cycles. The higher overpotential for Li nucleation and dissolution are a consequence of increased charge-transfer resistance associated to accumulation of SEI at the lithium-electrolyte interface. On the contrary, the LiF-Li electrodes showed much regular cycling and constant Li nucleation/dissolution overpotential, symptomatic of reduced new SEI formation with irreversible electrolyte consumption.

The beneficial effect of LiF coating on a metallic lithium electrode was further demonstrated in a rechargeable Li-metal battery employing a LFP cathode (Fig. 6). The charge-discharge test was performed at 0.2C

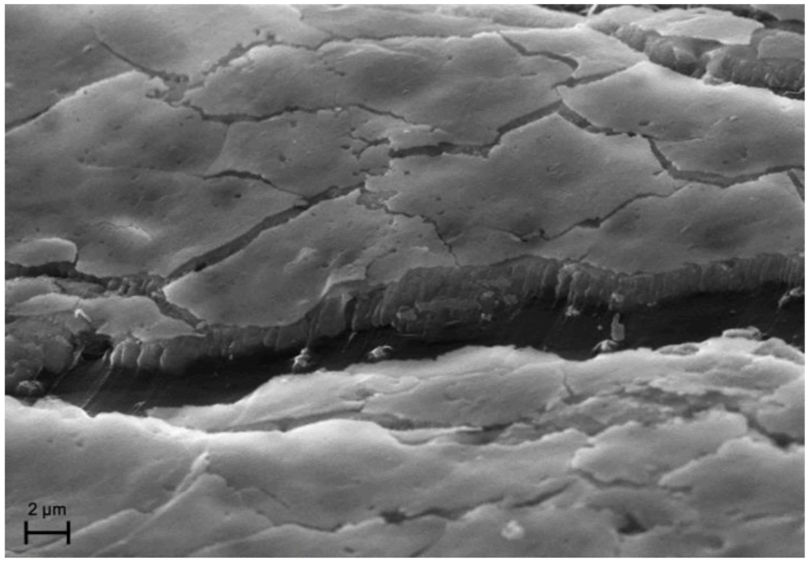

Fig. 3. SEM image of the LiF coating on the lithium surface.

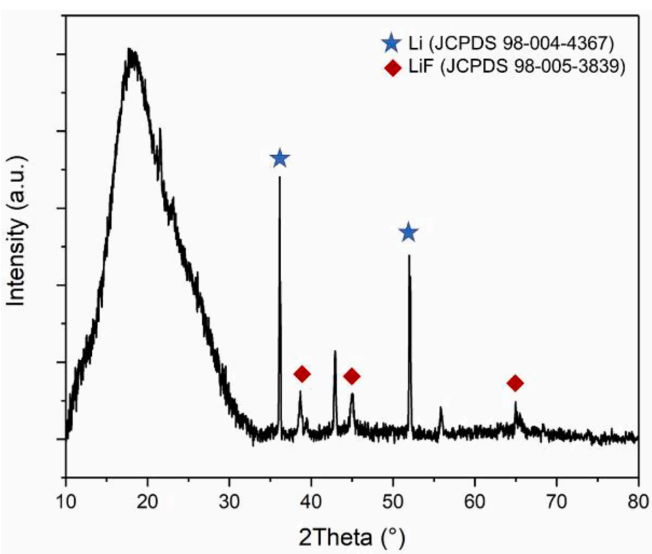

Fig. 4. XRD of the LiF-coated lithium. The broad peak at 20° is ascribed to Kapton tape used for covering the electrode during the analysis.

for 100 cycles in a coin cell (CR2032) in order to evaluate the improvements of the applied artificial SEI on both the specific discharged capacity (C_{sp}) and Coulombic Efficiency (CE). The LFP | LiF-Li battery showed much higher capacity retention respect to the bare lithium cell the quickly dropped to almost null specific capacity after 20 cycles. The improved cyclability of the LFP|LiF-Li cell is also demonstrated by the very regular CE (average CE 97.3%).

4. Background

The patentability search reports related to the Italian and the International patent applications cited five documents as background art:

D1: "Surface Fluorination of Reactive Battery Anode materials for Enhanced Stability" [1]

D2: CN 108 987 796 A [2]

D3: JP 2017 183256 A [3]

D4: "Recent progress in LiF materials for safe lithium metal anode of rechargeable batteries: Is LiF the key to commercializing Li metal

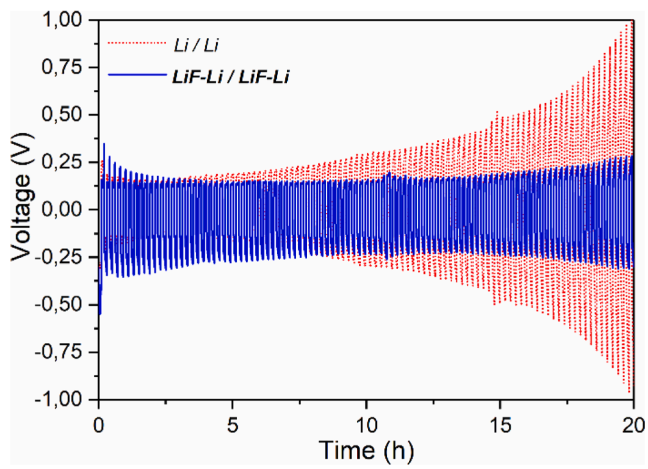

Fig. 5. Plating-stripping test of Li / Li and LiF-Li / LiF-Li symmetrical cells at 1 mA cm^{-2} of current density and 1 mAh cm^{-2} of lithium capacity.

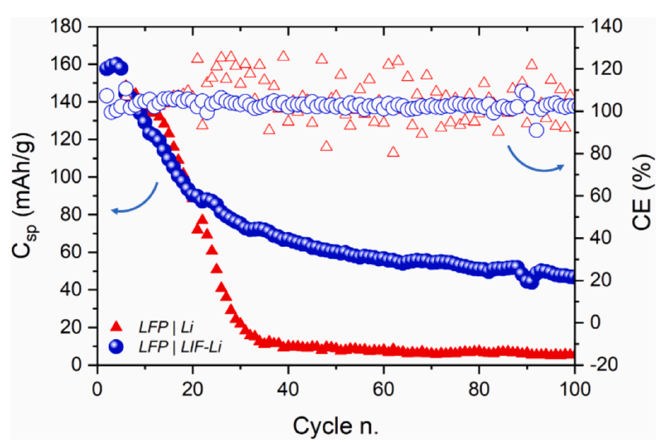

Fig. 6. C_{sp} and CE of the LFP-Li and LFP-LiF cells cycled at 0.2C.

Table 1
List of the classification codes used in the state-of-the-art patent search.

Classification symbol	Definition
C01D15/04	Lithium compounds • Halides
H01M10	Secondary cells; Manufacture thereof
H01M10/052	Li-accumulators
H01M4	Electrodes
C01D15/04	Lithium compounds • Halides

batteries?” [4]

D5: “The intrinsic behavior of LiF in solid electrolyte interphases on lithium” [5]

D6: “EP2871010 B1” [6]

D7: “EP3238290 A4” [7]

D8: “EP2983230 A1” [8]

D9: “EP2824739 B1” [9]

The search was carried out in the following technical fields: **H01M** (Processes or means, e.g. batteries, for the direct conversion of chemical energy into electrical energy), **C01G** (Compounds containing metals not covered by subclasses C01D or C01F), **C23C** (Coating metallic material; coating material with metallic material; surface treatment of metallic material by diffusion into the surface, by chemical conversion or substitution; coating by vacuum evaporation, by sputtering, by ion implantation or by chemical vapor deposition, in general) and **C01D** (Compounds of alkali metals, i.e. Lithium, Sodium, Potassium, Rubidium, Cesium, or Francium).

The examiner recognized the novelty requirement of claims 1 – 14, while claims 15 – 19 were deemed to be not novel by combining the technical features published in documents D1 and D2.

A surface fluorination process that forms a homogeneous and dense lithium fluorine (LiF) layer on reactive anodic materials, including in situ generation of fluorine gas, by heat treatment of a fluoropolymer (CYTOP), as precursor is disclosed in document D1.

In document D2 a lithium metal battery comprising an anode that includes a stabilized lithium strip, coated with a layer of lithium fluoride (LiF) is described. This layer has the function of preventing the oxidation of lithium and the formation of dendrites during the battery charging and discharging processes. The LiF layer is formed by heat treatment of the fluorinating agent, such as one or more perfluoro-resins [CYTOP, polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE)].

There is a difference between the state-of-the-art and the claimed invention because the invention contains a higher level of LiF (greater than 98% w/w) than the state-of-the-art.

Document D2 does not provide any further technical information than D1 because neither the direct reaction of lithium with fluorine nor the degree of purity of the LiF layer is mentioned in either of them.

Documents D6, D7 and D8 describe innovative inventions for high-capacity cathodes in lithium-ion batteries. Our technology can be matched with these inventions by substituting the graphite anode with fluorinated lithium. This substitution can result in a battery that is half the weight but has the same capacity, or a battery with double the capacity but the same weight.

When considering lithium-sulfur technology with a cathode as described in document D9, metallic lithium is the only suitable electrode due to its high capacity. To address the intrinsic problems related to the Shuttle Effect of the polysulfides in the cathodic side [9] and the dendrite formation on the anodic side, as explained in this study, innovative solutions are required to create a high-energy battery.

A state-of-the-art patent search can be carried out on Espacenet (a free online patent database provided by the EPO) using the following queries: cl = "C01D15/04/low" AND cl = "H01M10″ AND cl = "H01M4″ AND ftxt = "fluorine" cl = "C01D15/04/low" AND (cl = "H01M10/052″ OR cl = "H01M4") where cl stands for IPC or CPC (International or Cooperative Patent Classification) and ftxt stands for All text fields (Title, abstract, claims and description). The definition of the classification symbols used is reported in Table 1.

Table 2
List of queries used in FamPat database search.

No.	Results	Query
1	47	(FLUORINE)/TI/AB/CLMS/DESC/ODES/ICLM AND (C01D-015/04 AND H01M-010+ AND H01M-004+)/IPC/CPC
2	108	(C01D-015/04 AND (H01M-010/052 OR H01M-004+))/IPC/CPC
3	108	1 OR 2

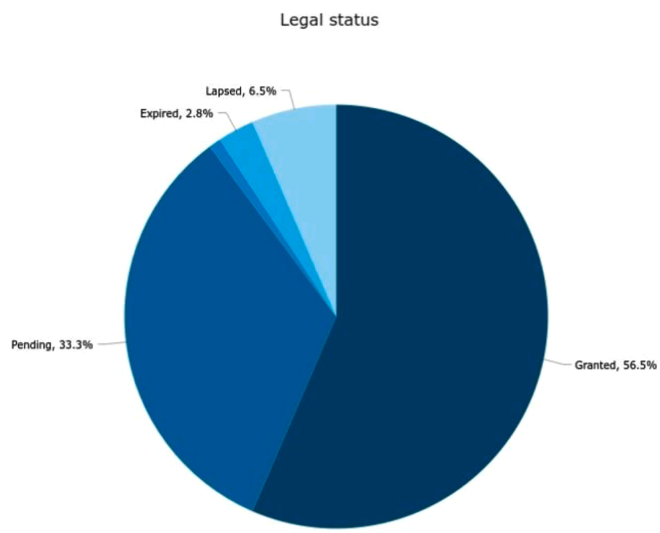

Fig. 7. Legal status of patent families (source: Orbit, accessed on 21 Sept. 2022).

A more precise and complete search can be performed on Orbit Intelligence (a fee-based platform provided by Questel), using FamPat as the reference database and the same above-mentioned keywords and classification codes. [10]

The search queries and results are reported in Table 2.

108 patent families were retrieved (97 are alive), of which 56.5 % are granted patents (see Fig. 7)

The filing trend of patent applications over the last ten years is reported in Fig. 8.

5. Application potential

This new technology belongs to the field of lithium-based batteries, that represents the 75 % of all the portable rechargeable battery market. Moreover, lithium batteries are widely used in large-scale energy storages centers (Gigafactory, <10 MWh) supporting other sources of renewable energies for the automotive (100 kWh). The energy storage lithium-based technology market was evaluated at $30bn in 2017 and prospections estimate a value of at least $100bn by 2025. Considering that a patent lasts for 20 years, our product allows to be competitive for all the duration of the patent and, consequently, would guarantee an income, from this completely innovative product, of around 10–20 times the production costs. Indeed, an estimation of the fluorination treatment for the active material of a commercial lithium disk for the coin cell batteries (ex. CR2032) is approximately 0.005€ (0.5 cent) and the profit margins are potentially significant.

There are three products/services that could be direct application of the patent: the treatment of lithium metal anodes; the sale of metal lithium anodes treated; the sale of lithium batteries containing treated metal lithium anodes. The treatment of metal lithium anodes according to the patented technology is certainly the most feasible application for creating a business case, assuming that in this case the reference customers would be directly the manufacturers and assemblers of batteries.

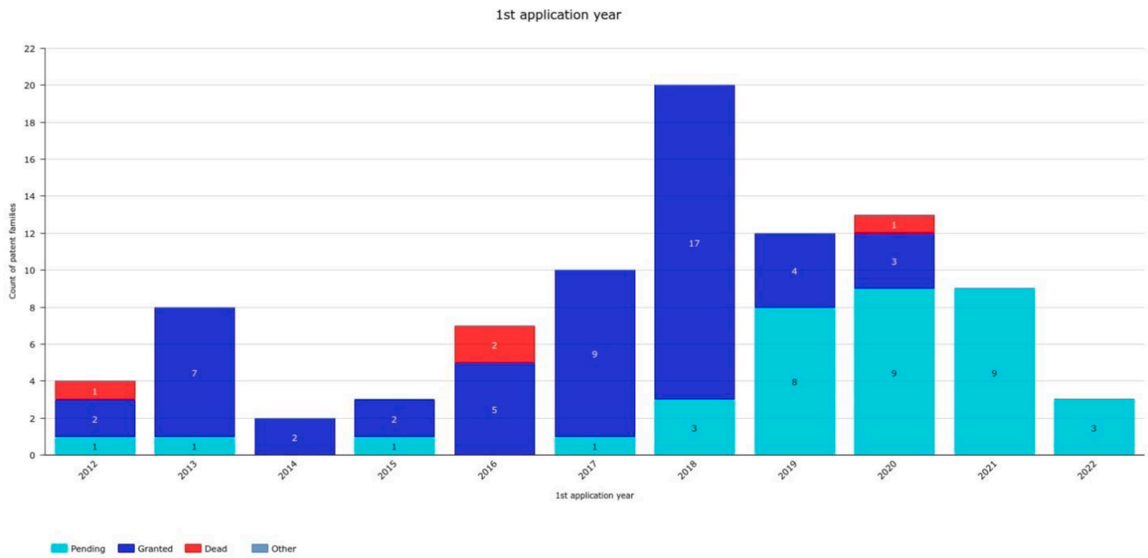

Fig. 8. Technology investment trend over the last 10 years (source: Orbit, accessed on 21 Sept. 2022).

Manufacturer R&D centers could be interested in the advantages of this patented technology but would expect that the metal lithium of the production should first be sent to a dedicated plant for the stabilization treatment before then being returned and introduced into the production chain without requiring changes to the production plants of manufacturers or assemblers. The development of a dedicated device that allows the treatment to be directly inserted into the automated process of battery manufacturing and assembly could also be investigated.

Ethics statements

No specific ethic statements.

CRediT authorship contribution statement

Eugenio Gibertini: Data curation, Methodology. **Piergiorgio Marziani:** Data curation, Writing – original draft, Writing – review & editing. **Massimo Barbieri:** Writing – review & editing. **Luca Magagnin:** Methodology, Supervision. **Maurizio Sansotera:** Conceptualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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