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The renaissance of lithium metal: SolidEnergy's role in the future of lithium batteries

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The pursuit of high energy density is at the heart of smartphones, wearable gadgets and electric vehicles — devices that are quickly becoming extensions of our bodies. Lithium, which is the lightest and most electronegative metal in the periodic table, is a natural choice as anode. However, because lithium metal is highly reactive it was sidelined during much of the 1990s and 2000s and replaced with Li-ion batteries that do not contain lithium metal. With recent advances in electrolyte, lithium metal is making a strong comeback. SolidEnergy was founded in 2012 during the turmoil of the lithium-battery industry crisis to introduce transformational changes in battery safety, energy density and a new business model. SolidEnergy is developing a renaissance technology, electrolyte and anode materials for safe and ultra-high-energy-density Li-Metal batteries. And because the Li-Metal batteries enabled by its materials can be manufactured using existing Li-ion manufacturing facilities, the company is also developing a renaissance business model by building an open ecosystem, strategically partnering with established companies to accelerate the commercialization of disruptive technologies in the battery industry. SolidEnergy's mission is to power people's lives, whether they are communicating with loved ones on a phone or driving with their family in an electric car.

The history of lithium batteries: Li-ion versus Li-Metal

In the past 30 years there has been tremendous progress in the lithium-battery industry (both Li-Metal and Li-ion), including new cathodes, safer coatings on separators and better cell engineering[1,2]. There were only a

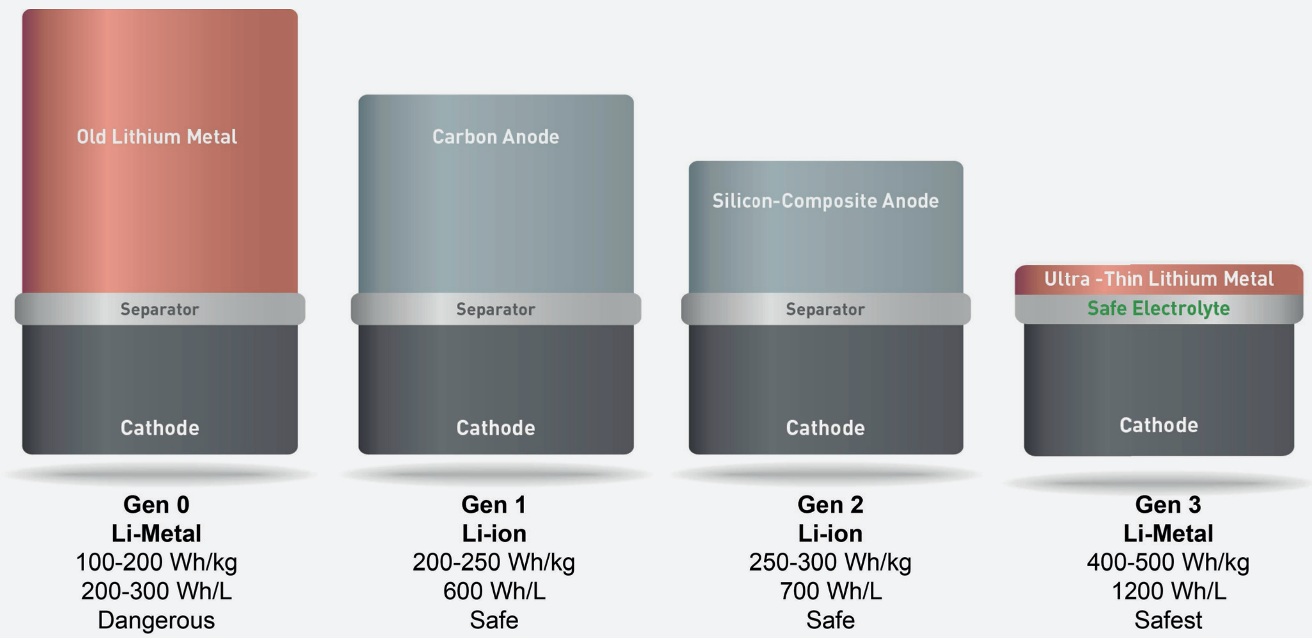

Figure 1 | The history of lithium batteries from an anode perspective.

few step-change developments in anodes and electrolytes, and the history of lithium batteries can be categorized based on anodes (**Figure 1**).

Given its low electronegativity (-3.04 V versus standard hydrogen electrode), low specific gravity (0.53 g/cm^3) and high lithium ion specific storage capacity (3,850 mAh/g), lithium metal is the ideal choice as anode. Since the 1970s, lithium metal has continued to demonstrate its high energy density in primary batteries for applications such as implantable medical devices, space exploration and oil field services. The first rechargeable lithium batteries were also demonstrated in the laboratory with lithium metal anodes and intercalation cathodes such as TiS_2, $LiCoO_2$, VO_x and MoS_2 by pioneers like Stanley Whittingham and John Goodenough[3]. The first commercial rechargeable lithium batteries (Gen 0 in **Figure 1**) were developed by Moli Energy using lithium metal anodes in the late 1980s and had energy densities in the range of 100-200 Wh/kg and 200-300 Wh/L[4].

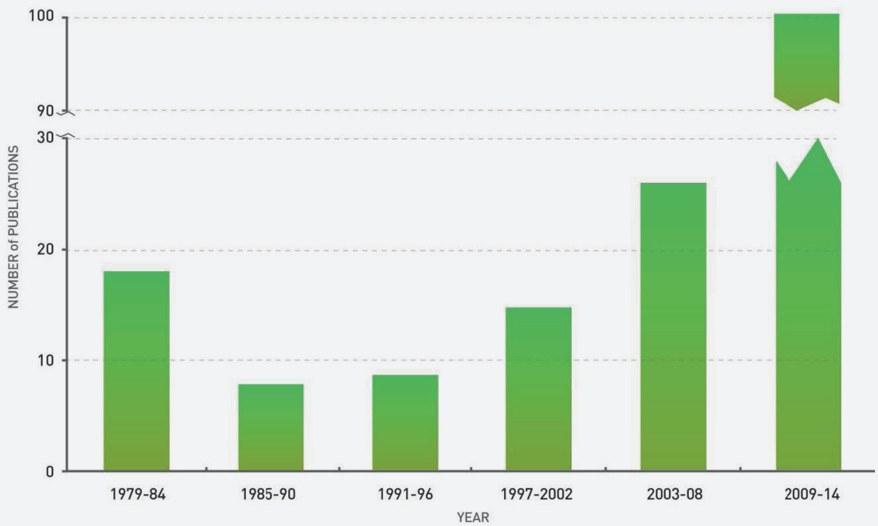

Figure 2 | The renaissance of lithium metal. The number of publications related to Li-Metal batteries (including those published on www.nature.com by Nature Publishing Group and in the following journals: *Journal of the American Chemical Society*, *Journal of the Electrochemical Society*, *Journal of Power Sources*, *Electrochimica Acta*, and *Electrochemistry Communications*).

However, there was a major flaw with the old Li-Metal batteries (Gen 0), and that was the formation of mossy lithium during charging (not a problem for primary batteries). During charging, fresh lithium metal is plated onto a lithium metal anode. When the electrolyte is an organic carbonate liquid, it reacts with lithium metal to form mossy, dendrite-like structures that can pierce through the separator and lead to an internal short and even explosions, causing serious safety concerns. In addition, the reaction between the electrolyte and lithium metal anode forms unstable solid-electrolyte-interphase (SEI) layers consuming both electrolyte and lithium metal, leading to low coulombic efficiency and requiring a thick lithium metal anode (typically 3 to 5X excess) to achieve an acceptable cycle life (>200), resulting in low energy density.

Given the concerns in both safety and low energy density, the industry moved away from Li-Metal and adopted a 'lithium-metal-free' Li-ion system, in which both the cathode and anode were intercalation compounds. Graphite, which has a lithium ion specific storage capacity of only 380 mAh/g (one-tenth that of lithium metal) but can allow lithium ions to intercalate and de-intercalate freely and form relatively stable SEI, replaced lithium metal as the new industry standard anode. Lithium exists in a Li-ion system only in ion form and not in metal form. Sony commercialized the first Li-ion batteries (Gen 1) by combining a graphite anode with a $LiCoO_2$ anode in 1991. Although Sony had safety issues of its own, its Gen 1 Li-ion batteries were a dramatic improvement over Gen 0 Li-Metal batteries in both safety and energy density (albeit much of the improvement in energy density came from better cathodes and cell engineering), and Gen 0 Li-Metal batteries commercialized by Moli quickly faded away.

Graphite-based Gen 1 Li-ion batteries gradually became mainstream throughout the 1990s, 2000s and even until today. In the mid-2000s, the industry tried to improve the specific capacity of graphite anodes by incorporating silicon in various forms to create silicon–carbon composite anodes with lithium ion specific storage capacity of up to 1,500 mAh/g. Although such silicon–carbon composite anodes face challenges with cycle life, volume expansion and unstable SEI, they are considered Gen 2 Li-ion batteries, offering significantly higher energy density both gravimetrically (Wh/kg) and volumetrically (Wh/L) compared to Gen 1 Li-ion batteries.

The development of all-solid-state Li-Metal batteries

Efforts to solve the mossy lithium formation in lithium metal/liquid electrolyte combination that plagued Gen 0 Li-Metal batteries continued in the 1990s and 2000s. The focus was to replace the liquid electrolyte with a solid electrolyte and create an all-solid-state Li-Metal battery. The solid electrolytes included polymer electrolytes, which were typically complexes of lithium salts with lithium ion conducting polymers such as polyethylene oxide (PEO)[5], and ceramic electrolytes, such as LiPON, thio-LISICON, $La_{0.5}Li_{0.5}TiO_3$, $Li_7P_3S_{11}$ and $Li_{10}GeP_2S_{12}$[6,7]. Both of these solid electrolytes are non-flammable and non-volatile and are significantly safer than organic carbonate liquid electrolyte.

The solid polymer electrolytes could be roll-to-roll solution processed on a large scale and were commercialized by companies such as Avestor, Bathium and Seeo. The solid ceramic electrolytes had to be vacuum deposited, an expensive technique more commonly found in the semiconductor industry, and were commercialized by companies such as Infinite Power Solutions, Cymbet and Sakti3. However, because of the low conductivity and poor electrode–electrolyte interfaces in solid electrolytes, solid-state Li-Metal batteries were restricted to either high temperature (>80 °C) or miro-size thin-film applications, thus could not be used in mainstream consumer electronics and only achieved limited use in niche electric vehicles.

Although the lithium-metal-free Li-ion battery continues to reign supreme, there is a limit to its energy density. Li-ion relies on intercalation anodes such as graphite and silicon–carbon composite, which are inert. The intercalation anodes only provide host structures for lithium ions but do not contribute to energy storage themselves and are considered 'deadweight'. This limits the energy density of Li-ion. Li-Metal, on the other hand, does not have such deadweight because lithium metal does not have any alien host

structure and consists purely of lithium ions.

Li-Metal can be divided into three categories: Li/intercalant cathode; Li/sulfur; and Li/air. The most ambitious of the three is Li/air, which has a potential for >10,000 Wh/kg (approaching that of gasoline), but it remains a long way from commercialization because of fundamental science issues. Li/sulfur has demonstrated nearly 500 Wh/kg in commercial cells and has been used in aerospace applications, in which lightness is paramount. But its volumetric energy density (Wh/L) is significantly less than Li-ion, and its bulkiness has prevented its application in consumer electronics and electric vehicles. Li/intercalant cathode has demonstrated that with a lithium metal anode it can increase the energy density (both Wh/kg and Wh/L) by 100% compared to a graphite anode and 50% compared to a silicon-carbon composite anode (**Figure 1**).

Whether the cathode is air, sulfur or high-voltage intercalant, the key enabling technology to all Li-Metal is the electrolyte — one that can enable stable cycling of lithium metal at high current density without the formation of mossy lithium. Since the late 2000s, there has been a renaissance in research on electrolytes for Li-Metal, as evidenced in the number of publications in this area (**Figure 2** shows that Li-Metal was a hot topic in the beginning and then faded away due to Li-ion and is gaining momentum again). These include novel lithium salts (including room temperature ionic liquids)[8] that have higher coulombic efficiency on lithium, additives that smoothen mossy lithium during plating[9], new approaches to salt:solvent ratio to improve coulombic efficiency[10], and novel materials and engineering techniques to build protective layers on lithium[11,12]. Gen 3 Li-Metal is a renaissance technology that builds upon the all-solid-state batteries developed in the 1990s and 2000s, and addresses the high temperature and thin-film limitations.

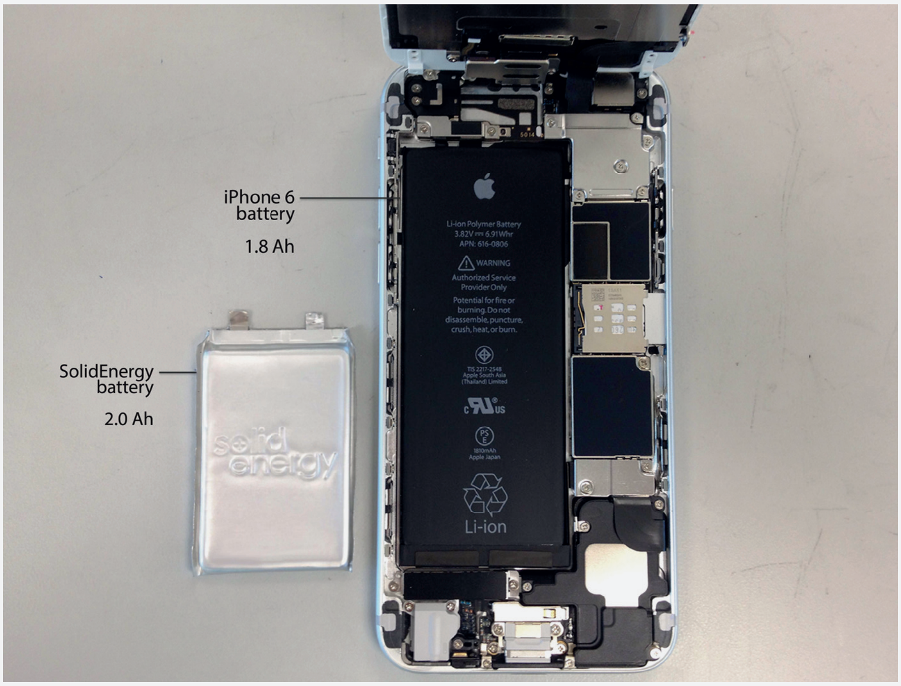

Figure 3 | Half the size. A SolidEnergy prototype battery (left) has 400 Wh/kg and 1200 Wh/L, twice that of an Apple iPhone 6 battery (right).

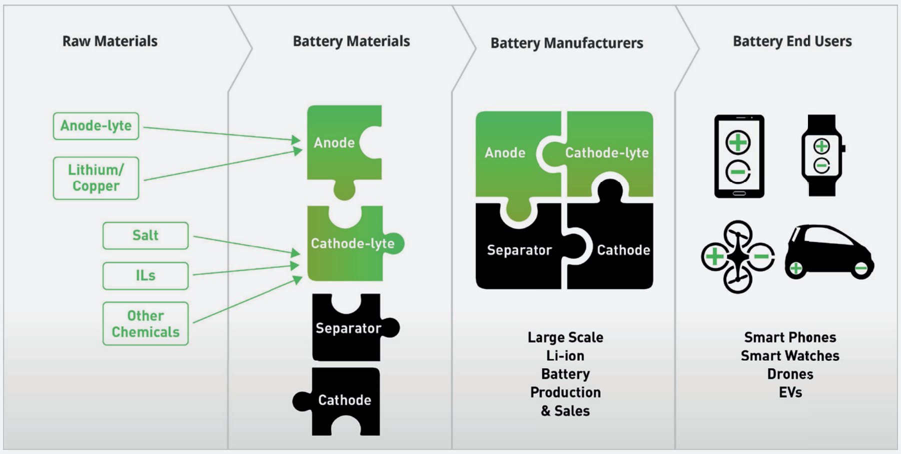

Figure 4 | The ecosystem in which SolidEnergy operates. SolidEnergy innovates at the materials level, not the manufacturing level (its contributions are in green).

The story of SolidEnergy

SolidEnergy Systems Corp. was incorporated in spring 2012 to develop and commercialize a safe and ultra-high energy density 'anode-free' battery (Gen 3 Li-Metal) using an ultra-thin lithium metal anode (the anode is so thin that it is almost anode-free) and a combination of solid polymer and ionic liquid electrolyte, a concept that was originally conceived at Massachusetts Institute of Technology (MIT). Unfortunately, 2012 saw one of the worst meltdowns in the history of the lithium battery industry, and many large Li-ion battery and electric-vehicle manufacturers filed for bankruptcy after having raised tens of billions of dollars. It was an adverse environment for a young fledging company, but SolidEnergy persevered and rose out of the ashes. SolidEnergy took a worldwide exclusive license from MIT, formed strategic partnerships with the reborn A123 and leading consumer electronics companies, and raised venture investment from major auto companies. In a little more than one year, SolidEnergy demonstrated in a real 2 Ah prototype battery (not just based on simulation results) 400 Wh/kg and 1200 Wh/L, twice the energy density of an Apple iPhone 6 battery (**Figure 3**), and operating at room temperature, all independently verified by third parties and at a speed unprecedented in the industry.

SolidEnergy's role in the ecosystem

In addition to developing a renaissance technology SolidEnergy also adopted a renaissance business model. It has learned many important lessons from the perils of its predecessors, many of whom started with a disruptive technology but sidetracked to focus on battery manufacturing. These predecessors tried to compete with established companies in an extremely capital intensive arena that is red-hot crowded and with severe overcapacity. At the same time, established companies were too

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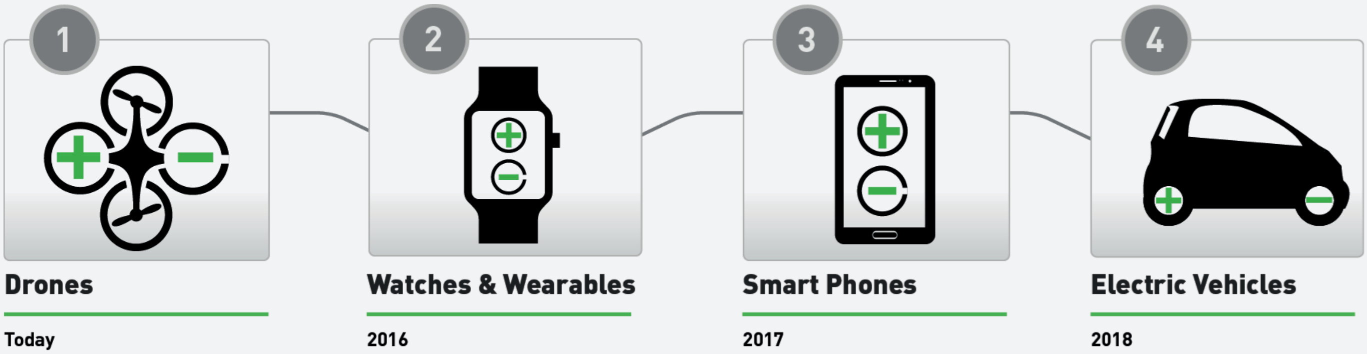

Figure 5 | SolidEnergy's roadmap for the anode-free battery (Gen 3 Li-Metal).

conservative to put serious resources behind disruptive technologies. As a result, the lithium-battery industry has seen many incremental improvements, but rarely disruptive ones.

SolidEnergy disciplinarily focuses on the area in which it can create the most value, which is key enabling battery materials. It innovates at the materials level, not the manufacturing level, but the batteries enabled by its materials can be manufactured using existing Li-ion manufacturing capability. This allows it to avoid massive infrastructure investment duplicating what the industry already has, leverage an established ecosystem, and efficiently capture the highest value.

Figure 4 shows SolidEnergy's business model and how it fits in the overall ecosystem. It acquires and processes raw materials from its strategic partners in chemical and equipment manufacturing. The company develops two key enabling battery materials: the anode, which consists of anode-lyte coating on lithium/copper; and the cathode-lyte (anode-lyte and cathode-lyte are two components of electrolyte), which consists of salts, ionic liquids and other chemicals. These two battery materials are then supplied to the battery manufacturers with a separator and a cathode to form complete batteries. SolidEnergy does not manufacture batteries, instead it provides key enabling battery materials.

SolidEnergy works with battery end users such as consumer electronics and auto companies to finalize the battery design, and with battery manufacturers to develop the engineering and manufacturing processes. This open ecosystem integrates SolidEnergy's anode-free battery design and materials seamlessly into the end user experience while minimizing infrastructure investment and industry redundancy.

Many of SolidEnergy's predecessors failed because they targeted exclusively electric vehicles and ignored consumer electronics. Electric vehicles have the toughest performance and cost requirements and the longest development cycle. For example, electric vehicles require eight-year warranty and smartphones are replaced every two years. But most of today's successful electric-vehicle battery manufacturers built strong foundations in consumer electronics first. The fast innovation cycle and relatively easier performance and cost requirements in consumer electronics make it an ideal platform to develop, demonstrate and optimize a new battery technology before it becomes mature enough for electric vehicles.

SolidEnergy's vision for the future

The commercialization roadmap for SolidEnergy's anode-free battery touches several markets, including drones, watches & wearables, smartphones and electric vehicles (**Figure 5**). The sequence increases in both market size and entry difficulty. Drones and watches & wearables value high energy density but have relatively small capacity and are great beachheads to test a new battery technology. Smartphones and electric vehicles value scale and cost in addition to high energy density, and demand much higher capacity, but are fertile markets in which to build a large company in the long term.

Although these markets may seem dramatically different and the batteries may have different form factors and different manufacturing processes, SolidEnergy's key enabling materials are largely transferrable throughout and can ride the wave of innovation in cathodes and other aspects, giving them flexibility and longevity. SolidEnergy is introducing its materials for drones this year; watches & wearables in 2016; smartphones in 2017; and electric vehicles in 2018.

It is now 2015. Li-ion can no longer satisfy our insatiable thirst for higher energy density, and even with the best engineering it is approaching its theoretical limit. If we refuse to let battery technology limit our desire for smarter devices and cleaner transportation, we must focus on the next practical solution, Li-Metal. Although challenges to Li-Metal remain daunting, the current renaissance in technology and new business model give us confidence that Li-Metal will soon reclaim its rightful spot in the industry.

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