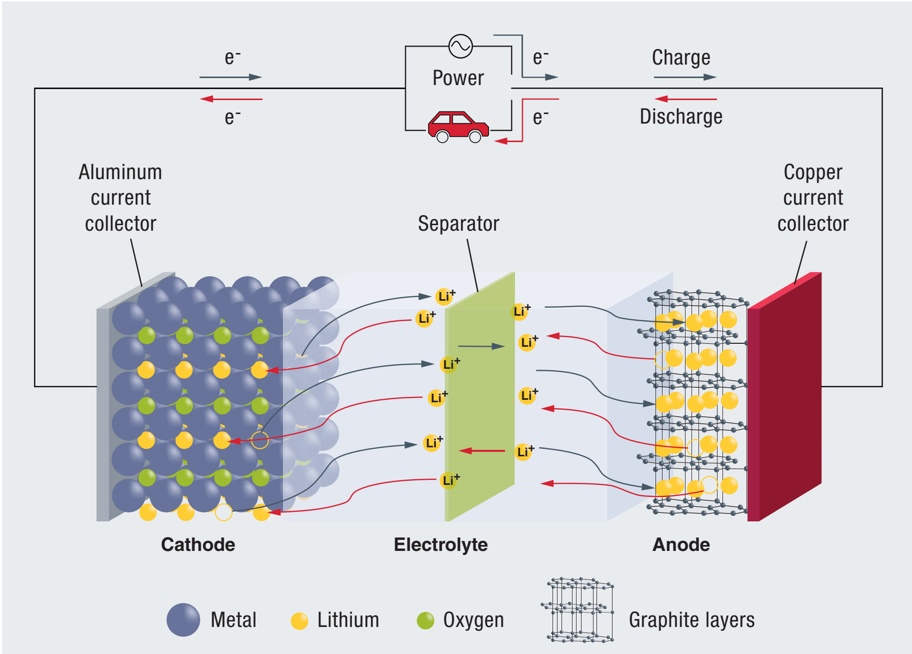
Moly to boost batteries?

When developing sustainable technologies such as renewable energy solutions and electric vehicles, power storage is as crucial as power generation. To this end, improving battery performance is an area of enormous scientific interest. Numerous studies show that molybdenum disulfide composites could play a key role in increasing batteries' electrical power, energy storage capacity, recharging speed and stability.

Laptops, mobile phones, electric scooters and a plethora of other rechargeable devices all depend on lithium-ion/graphite (LIB) batteries. But some scientists and urban planners imagine a future where batteries could do much more e.g. power airplanes or even entire cities. These promising ideas, as well as longer ranges for electric vehicles, remain limited by the relatively low storage capacity of the graphite anode in commercial LIBs. However, researchers may finally have a robust solution to this problem. Certain molybdenum disulfide (MoS_2) composite anodes have been found to have two to three times the storage capacity of graphite. Therefore, molybdenum-containing compounds in batteries could offer significant improvements over currently available energy storage capacity.



A lithium-ion battery cell with lithium-metal (Co, Ni, Mn, or Al) oxide cathode and graphite anode. During charging, electrons (e^-) travel from the cathode round the external circuit to the anode and lithium ions, Li^+ travel through the electrolyte. The opposite movement occurs when the battery is used to power a device. In a MoS_2 cell MoS_2 or a composite replaces the graphite anode. [1]

Molybdenum disulfide history in batteries

From electric shavers, to drones, to electric vehicles, batteries are ubiquitous; but, what *is* a battery, and how is molybdenum involved? A battery is a cell or set of connected cells that convert chemical energy to electrical energy. Each cell contains a negative terminal, the "anode," and a positive terminal, the "cathode." Both the anode and the cathode, known generically as "electrodes," are immersed in an electrolyte that conducts electricity. For example, sulfuric acid is the electrolyte in the traditional lead-acid battery installed in vehicles around the world. These batteries contain lead electrodes that are not only extremely heavy but also have other drawbacks, including low energy density and potential environmental exposure. These disadvantages spurred the development of new rechargeable-battery designs in the 1970s and 80s. An early example is the nickel metal hydride (NiMH) battery, which depends on an optimal exchange of hydrogen ions. 'Lithium-ion' batteries, which supplanted much of the market for NiMH batteries, provided improved life, greatly improved energy density and reduced life-cycle cost. As a result, lithium-ion batteries supply power to most laptops and other consumer devices today.

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Lithium-ion/graphite batteries power most common, rechargeable devices.

This is where molybdenum comes in. An early (1980s) lithium rechargeable battery design used a MoS_2 anode, delivering more energy, without memory effect, than the existing Ni-Cd battery, which was the standard rechargeable of the day. Unfortunately, the design's use of highly reactive lithium metal resulted in overheating and fires. And, the battery lost power after relatively few charge/discharge cycles as the Li-MoS_2 deteriorated, limiting its service life. Commercial interest in MoS_2 waned, but recent research suggests that it might provide the next breakthrough in energy storage.

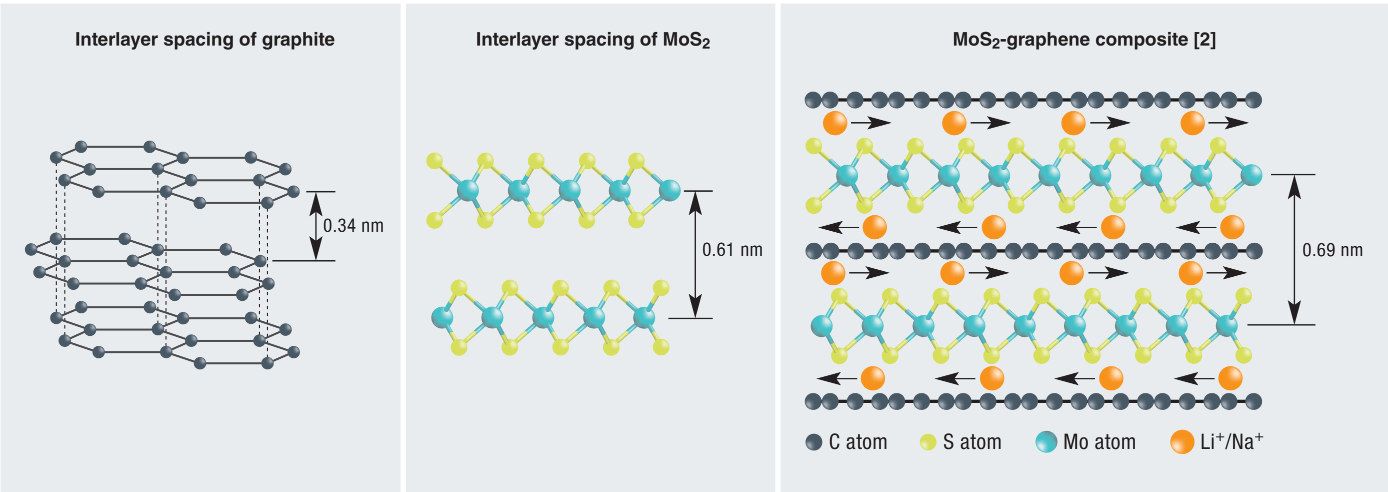
MoS_2 and carbon: better together

In the operation of a battery cell, the greater the number of ions stored, the larger its capacity. Moreover, the faster these ions travel, the more efficient the cell. Today, most LIBs have a lithium-metal (Co, Ni, Mn, or Al) oxide cathode and a graphite anode. Graphite, made of layers of carbon atoms, has better stability and conductivity than MoS_2, (also a layered material), but graphite cannot store as many lithium ions between its layers. The wider interlayer spacing of MoS_2 provides nearly twice graphite's storage capacity, as shown on the graphic below.

Rechargeable battery types

Feature	Lead-acid	LiCo	LiNiMnCo	$NiCoAl_2O_3$
Anode (-)	Pb	Graphite	Graphite	Graphite
Cathode (+)	PbO_2	$LiCoO_2$	$LiNiMnCoO_2$	$LiNiCoAlO_2$
Energy density (kwh/kg)	30 – 50	150 – 250	150 – 220	200 –260
Cycle life	200 – 300	500 – 1,000	1,000 – 2000	500
Applications	Automotive batteries	Dominant for laptops, cameras, mobile phones, but likely to be replaced by LiNiMnCo.	Electric vehicles, in the future also consumer electronics and stationary.	Electric vehicles, may also be replaced by LiNiMnCo in the future
Advantages	Inexpensive	Long tradition, good energy density	Low cost, safe, long life	Low cost, high energy density
Disadvantages	Low energy density, heavy, toxicity	High cost, limited availability, toxicity	Lower energy density	Less safe

When MoS_2 layers are stacked together with layers of highly conductive nano-materials such as graphene or carbon nanotubes the anode performance further improves. These 'composite' electrodes are superior to electrodes made of either material separately. They combine the desirable properties of both and more: the larger Li^+ storage ability and fast ion transport of MoS_2, and the exceptional electrical conductivity of graphene, without the accelerated degradation of ❯



Layer structures and interlayer spacing of graphite, MoS_2, and a MoS_2-graphene composite. The gap between layers, which can accommodate ('intercalate') lithium or sodium ions, is almost twice as wide for MoS_2 as for graphite. A composite further improves the capacity for Li^+ ion storage.

the early MoS_2 batteries. In fact, lithium-ion composite battery technology can provide *twice* the initial capacity of a corresponding MoS_2 battery, according to the data on the right, and the composite has exceptional cycling capabilities as shown in the figure below.

Developing technologies: lithium-air and sodium-ion batteries

New research suggests MoS_2 may also play a role in developing battery technologies, including Li-O_2 (air) and sodium-ion batteries. While these technologies are not yet commercial, electrodes using both MoS_2 or MoS_2/graphene composite have demonstrated excellent performance in laboratory trials. In Na^+ batteries, MoS_2's wider interlayer spacing compared to graphite is essential to accommodate the bigger Na^+ ion (0.10 nm radius, cf. Li^+ 0.076 nm). Furthermore, the storage capacity of a sodium-ion cell with the composite electrode is greater than the sum of capacities for cells with individual MoS_2 and graphene electrodes, as shown by Xie et al. (2015) [5].

Summary of electrochemical performance data for various LIB anode materials [4]

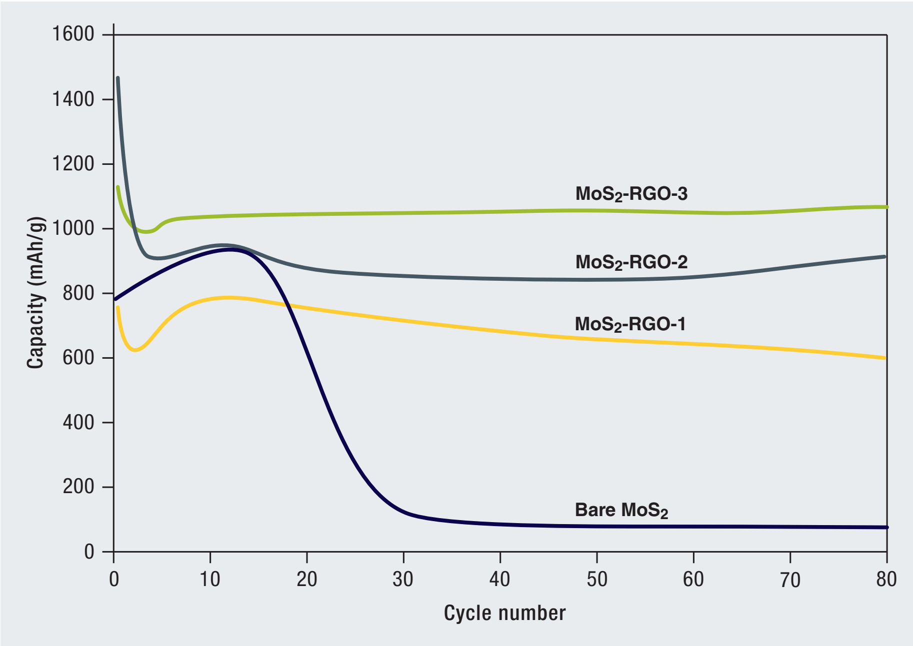
Anode materials	Theoretical specific capacity mAh/g	First discharge capacity mAh/g	First charge capacity mAh/g	Reversible capacity after (n) cycles mAh/g
MoS_2	669	1062	917	907 (50)
MoS_2-GNS*	669 – 1675	1300	2200	1290 (50)
Graphene	372 – 1116	945	650	460 (100)
Graphite	372	320	320	240 (20)

* MoS_2-Graphene nanosheet composite

From the laboratory to production

Sustainability is an important consideration in the development of new technologies. Life Cycle Inventory datasets, shown on page 16 for molybdenum, support assessment tools such as Life Cycle Costing (LCC) and Life Cycle Assessment (LCA). LCC measures the differing total life cycle costs between battery technologies performing similar functions. Likewise, LCA evaluates environmental impacts of batteries on a life cycle basis over production, distribution, use and end-of-life. Outcomes of such assessments are increasingly important in decisions to upscale to commercial production.

Moving from the laboratory into the up-scaled commercial world is challenging for new technologies – especially for those that use nanomaterials like the atom-thick layers required here. The processes to make composite sheets of nanoscale graphite and MoS_2 combined are different from those used to make sheets of graphite and MoS_2 individually.



The capacity development with increasing number of charge and discharge cycles for MoS_2-RGO (reduced graphene oxide) anodes and a bare MoS_2 anode. While the bare MoS_2 anode loses much of its initial capacity in this test after 15 to 20 cycles, the composite anodes are much more stable. [3]

Considering the potential economic impact of these composite electrodes when commercialized, many routes for scalability are being explored in laboratory studies. For example, composites consisting of stacked MoS_2 nanosheets embedded in a matrix of amorphous carbon, were prepared hydrothermally by mixing aqueous solutions of the MoS_2-precursor ammonium tetrathiomolybdate and a carbon source (resorcinol, formaldehyde and sodium carbonate) followed by autoclaving and calcination by Das et al. (2012) [6].

In an ingenious one-step procedure, a mixture of glucose and ammonium tetrathiomolybdate was thermally decomposed, thereby creating glucose bubbles and, ultimately, MoS_2 nanoflakes in graphene by Fei et al. (2018) [7]. Other approaches use carbon nanotubes or graphene as "seeds" on which to grow ❯

MoS_2. Each of these approaches has produced impressive results, and all have the potential for process scalability.

Unlocking future potential

The challenge is a battery technology able to store ever more electricity, provide ever more power, and recharge ever more quickly. Promising laboratory results indicate that MoS_2 could play a role in a future battery-based economy. To satisfy the energy demands of rising populations and growing cities, while reducing the amount of carbon released to the atmosphere, means that more efficient and environmentally friendly ways to generate and store energy are needed. With commercial scalability, MoS_2 composite electrodes could play an important role in meeting these energy-storage challenges. (Philip Mitchell)

Batteries containing MoS_2 could one day help to increase the range of electric vehicles and maybe power entire cities. © iStockphoto.com/urbancow

Permissions and references in article

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