



Green Li-Ion Batteries through
Electrode Electroless Deposition



SOLVAY

asking more from chemistry®



LIFE+ GLEE

Layman's Report



LIFE12 ENV/IT/000712



A Sustainable Technology for the Manufacturing of Li-Ion Batteries

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The Li-Ion Battery Marketplace

There are three main factors behind the enormous success of lithium ion batteries. The first is the continuous development of devices adopting this technology such as smart devices, laptops and tablets, which require batteries with increased power and storage capacity. The second is the continuously growing worldwide need for energy and clean resources that are able to contain the increased CO₂ emissions; for example, photovoltaic plants need batteries that are able to store and release the accumulated energy while operating. The last factor is conditioned by the development of energy systems which will eventually allow for the complete substitution of combustion-engine vehicles with hybrid or electric ones. Li-Ion batteries represent the best solution for all of these factors and more due to the multiple advantages offered

over traditional rechargeable ones. Not only they are much smaller and lighter, but they provide increased energy density and power. This is why they get such attention both in the research and applicative fields. However, there are some health and safety concerns linked to their vast use. As of today, the cathode production process requires the use of the toxic solvent NMP, which is dangerous to human health. The European Community, through its REACH regulation, has been encouraging the progressive substitution of this solvent until its complete elimination in each field of use.

LIFE+ GLEE

The Project

The goal of the LIFE+ GLEE Project is to demonstrate the effectiveness of a sustainable process which substitutes NMP with a harmless solvent such as water during the production of the cathode. Advantages, aside from the elimination of toxic risks, include reduced production costs linked to the NMP solvent recovery and re-purification processes.

A further, critical objective consists in showing how batteries produced with this process perform better compared to those produced with current technologies.

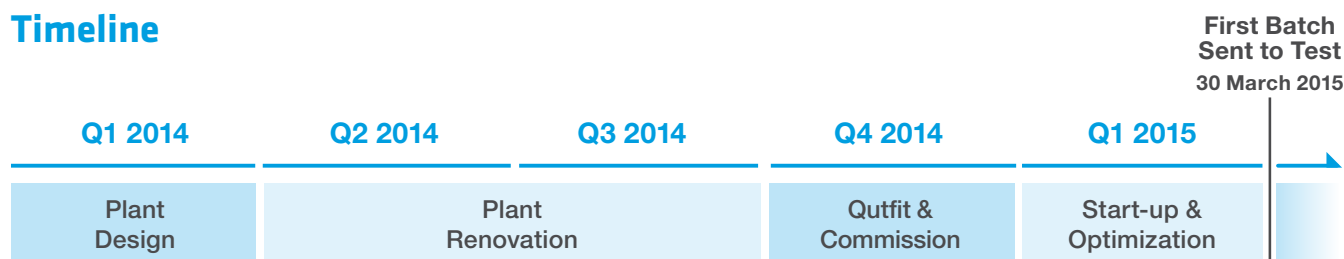
Both production and testing of this innovative technology will take place in the new pilot plant built within the Solvay Specialty Polymers R&I Center at Bollate, Milan (Italy). Produced under real industrial conditions, these materials will be available for evaluation by battery makers and research organizations.

The LIFE+ GLEE project is supported by the European Commission via funding from the LIFE financial instrument of the European Community.



Coordinator	Solvay Specialty Polymers
Project reference	LIFE12 ENV/IT/000712
Duration	02.09.2013 – 31.03.2016
Total budget	1.700.989 €
EU contribution	593.400 €
Project location	Bollate (MI), Italy
Website	www.solvay-lifeglee.com

Timeline



The Team

Steering Committee	The LIFE+ GLEE Project is supervised by a high level Steering Committee composed by 4 Senior Managers of both Solvay Specialty Polymers and Solvay Corporate.
Project Manager	Maurizio Biso (Lithium-Ion Batteries Researcher) is the LIFE+ GLEE project manager. The LIFE+ GLEE project belongs to the worldwide Solvay Open Innovation organization with the target of keeping perfect balance between technical results and dissemination and collaboration actions.
Process Development	The responsible of New Technology Development Lab and the inventor of the GLEE technology will represent together with his team the core competencies of the LIFE+ GLEE by developing the process and running the plant when operational. Following an Open Innovation approach, the Team is working in close contact with the Politecnico of Milano, to bring additional scientific insight in the LIFE+ GLEE technology.
Technology	Three experienced engineers are assigned to the project in order to scale-up the technology from lab- to industrial-scale conditions. Under their responsibility there will also be the planning of a number of sustainability measures to minimize the project carbon footprint and overall environmental impact of the initiative.
Testing & Quality	This team will contribute to test the output of the pilot plant and interact with external labs to have independent validation. In addition, this group will be in charge of liaising the LIFE+ GLEE project with the many European projects and initiatives on Lithium ion batteries.
Engineering & Infrastructure	Several professionals worked at different levels to the building of the new and customized GLEE pilot plant.
Monitoring	A special committee will be assigned to assess the environmental impact and carbon footprint of the project.
Communications	The project has the objective of communicating in a comprehensive way with a very wide range of stakeholders. The Marketing and Communication Team works very closely with the LIFE+ GLEE Team in order to ensure visibility and support all GLEE activities.
Public Relations	Special attention is and will be given in the links and involvement of the project's Stakeholders during the whole project's duration.

60Seconds
with **Francesco Triulzi**
Specialty Polymers Alternative Energy R&I Manager

“We knew of the health issues caused by NMP. It is a well-known issue in the Li-Ion battery market and is one that many R&I teams around the world have been trying to address, but without a final industrial solution.” In brief, NMP is dangerous for human health and reproduction. And, though it is not present in the final battery in contact with end-users, it is largely used in the Li-Ion batteries manufacturing process and creates an exposure risk for workers.”

“In late 2011, we hired a researcher with expertise in metal deposition processes. Using water as an NMP substitute was an impossibility until we identified a way to coat the particles to protect them from the water but still allow the battery to perform as expected.”

The Technology

The Innovative Idea

Cathodes Active Materials (CAM), the main components of the cathode, are of paramount importance for the operation and performance of Li-Ion batteries. CAMs promote lithium ion exchanges leading to the functioning of the battery itself. Today, CAMs are coated on an aluminum foil with a binder, typically PVDF, dissolved in NMP. The combination of these materials constitutes the electrode. Because CAMs are so critically important, there are great efforts in the industry to develop new technologies to improve battery power and energy density. However, these developments are impeded by

CAM's sensitivity to water and to their low resistance in aggressive environments.

The LIFE+ GLEE technology perfectly addresses this issue. It provides a simple method to coat the CAM with a protective layer which prevents water contact and at the same time improves the CAM's resistance to the aggressive components which are present in the battery.

The Current Situation

Li-ion battery slurry production uses *N*-Methyl-2-pyrrolidone (NMP)

The Alternative

Replace NMP with water



The Problem

Water corrodes Cathode Active Materials (CAM)

The Solution

Protect the CAM with water-proof, Li-ion permeable barrier technology

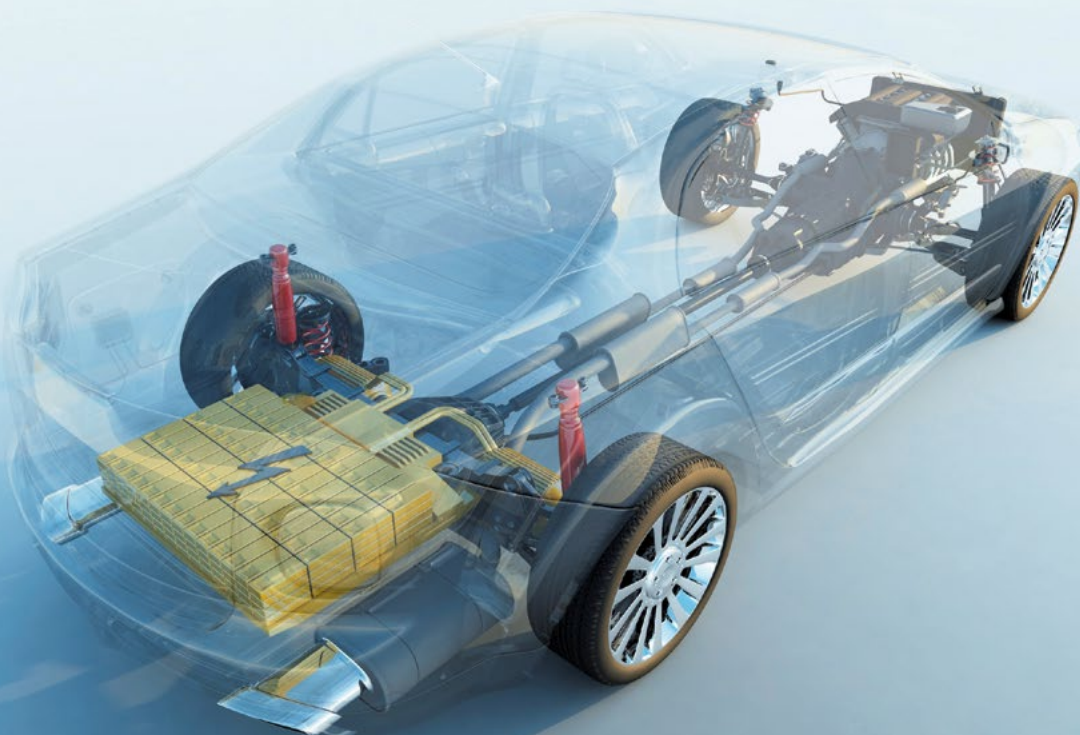
The Added Benefits

Protects against additional corrosive elements, improving performance and extending battery life

Reduces manufacturing costs associated with NMP solvent recovery and re-purification processes

The Solvay Commitment

To bring this technology from laboratory testing to commercial viability in a state-of-the art production facility



The coating process of a water-sensitive material is not difficult. In the case of cathode active materials, the challenge is to preserve lithium ions' intercalation and de-intercalation capability in their structure to maintain full battery functionality.

In order to obtain this result, the LIFE+ GLEE technology takes advantage of a coating which is permeable to lithium ions and impermeable to water and other aggressive chemicals. This paves the way to the utilization of an innovative, water soluble, PVDF-based binder which has been developed in Solvay Specialty Polymers laboratories. These innovative properties can be obtained only through accurate control of the coating process.

The immediate advantage of the LIFE+ GLEE technology is the elimination of the solvent NMP in the cathode manufacturing process by substituting it with aqueous formulations.

Moreover the protective layer increases CAM's resistance towards electrolytes thus solving the issue related to CAM instability in aggressive environments and at the same time improving battery performance.

Standard Li-Ion Battery



Alternative Li-Ion Battery



The Innovative Idea

Develop a coating that **will protect the CAM from water** but also allow the transmission of lithium ions



LIFE+ GLEE Technology



The CAM Protection Process

Cathode active material (CAM) powders are coated by using an electroless deposition process which consists of three steps:

Activation

To start the process, the CAM has to be activated through the adsorption of a catalyst (e.g. Palladium ions). To do this, the CAM is dispersed in an aqueous solution containing these catalysts which are attached to its surface due to a process called adsorption. This step activates the CAM coating process.

Protective layer deposition

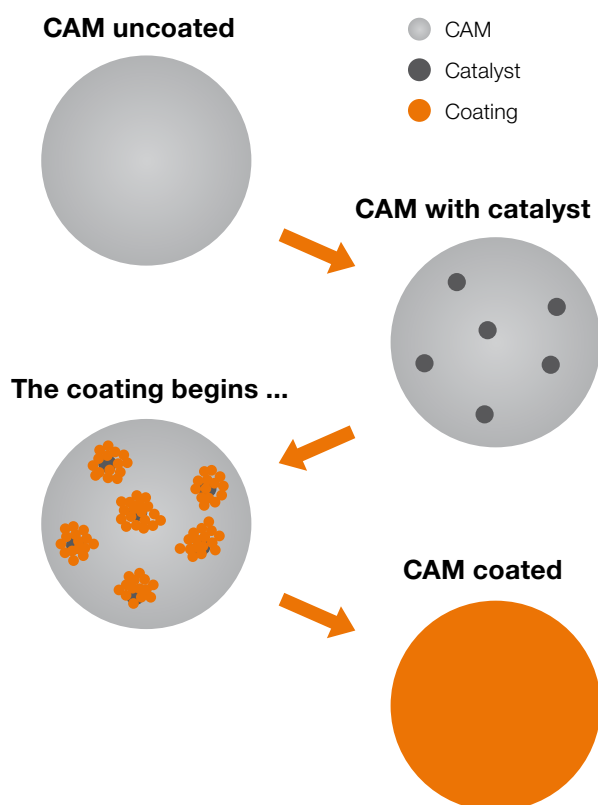
The activated CAM is then immersed in a deposition bath which is an aqueous solution containing metal ions which will work as the CAM covering. These metal ions start to deposit close to the catalyst particles and the coating will grow until the CAM is completely coated.

Coating finalization through thermal treatment

Before being used in the cathode production of Li-Ion batteries, the CAM has to be dried at the end of the coating process. This step is carried out by filtering the CAM powder and by drying it at high temperature.

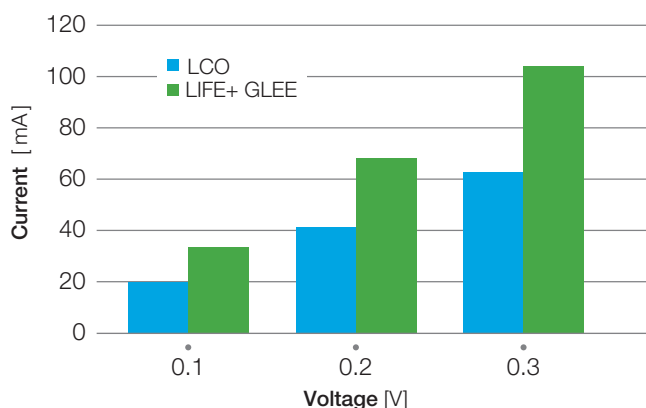
Now the powders are ready to be used in the production of a cathode for a Li-Ion battery.

Coating Process



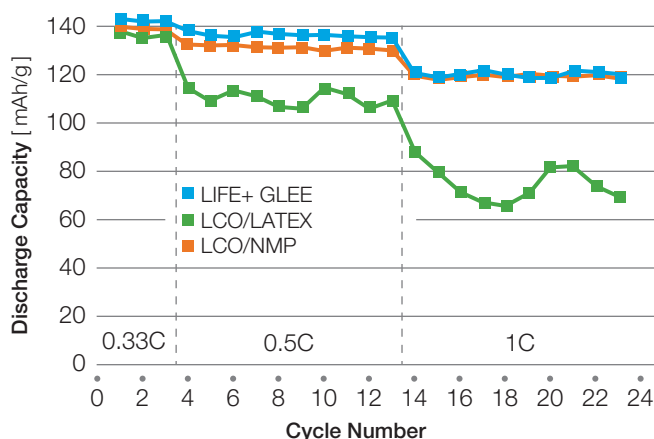
Lithium ion Batteries Performance

CAMs produced by using LIFE+ GLEE technology have superior performance than unprotected CAMs when the electrodes are prepared in an aqueous solution. Performance results are similar to the current technology based on the use of a toxic solvent.



Graph I/V (current/voltage) of a traditional CAM compared with a metallized one with technology LIFE+ GLEE.

The electrical current response is always superior for the metal-coated CAMs demonstrating better electrical properties.



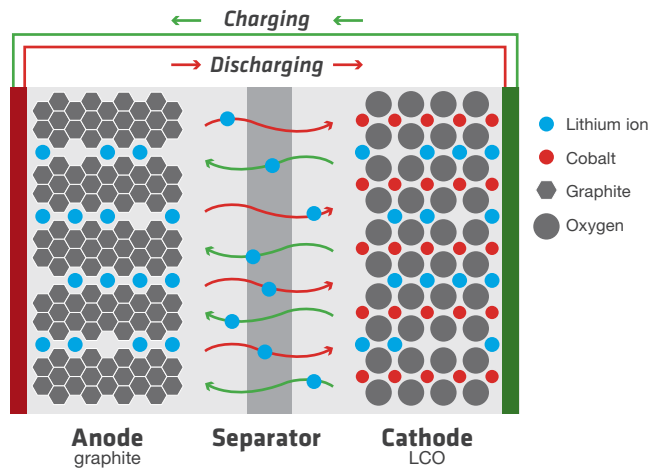
Graph of discharge capacity as a function of number of cycles (charge/discharge) at different discharge rates.

The previous graph demonstrates that the material processed through LIFE+ GLEE technology has better performance with respect to both an electrode prepared by using NMP (organic solvent) and an electrode prepared in aqueous solution if the CAM is not covered by the protective layer. In this last scenario, battery performance is very poor and this demonstrates that without using the LIFE+ GLEE process, the substitution of the toxic solvent NMP with water is impossible.

Lithium ion Batteries Configuration

In the classical configuration a Li-Ion battery is made of a cathode, an anode and a separator which divides the two.

The battery operating mechanism consists in the cyclic migration of lithium ions among the two electrodes (cathode and anode).



CAMs are coated with a binder, usually Polyvinylidene Fluoride (PVDF), and a conductive additive (CA), generally carbon black or graphite to improve the electrical conductivity of the electrode, on thin metal foils that act as current collectors (typically Al and Cu).

Lithium ions move in the electrolyte interacting with cathodes and anodes: active materials have to intercalate and de-intercalate lithium ions in their molecular structure or have to react reversibly with lithium ions.

Located inside the battery, the electrolyte is typically a liquid with dissolved salts which increases the ionic conductivity. The electrolyte needs to have a good ionic conductivity but no electrical conductivity because this could cause an internal short circuit.

In a standard battery, a separator is used to physically separate the anode and cathode in the electrolyte solution to prevent an internal short circuit. However, the separator is permeable to the electrolyte in order to maintain the desired level of ionic conductivity.

Carbon-based materials (conductive additives) are used to improve the electrode's electrical conductivity and create a continuous network of filling the pores between the CAM particles.

The function of the polymeric binder in the electrode is to link together the different components in order to create a mechanically and chemically stable network.

The most widely used binder for cathodes is PVDF. It is a high-performance partially-fluorinated polymer with excellent thermal, chemical and electrical stabilities.

This polymer grants good electrochemical performance and excellent adhesion among the materials which forms the electrode and the current collector.

The Pilot Plant

The LIFE+ GLEE pilot plant is located in the Solvay Specialty Polymers HQ of Bollate (Milan), one of the most advanced Research & Innovation centers in the Solvay group. The site, which hosts more than 300 employees, includes laboratories specialized in the development of innovative solutions for sustainable technologies in the photovoltaic, Li-Ion battery and hydrogen markets. The GLEE plant covers an area of nearly 300 sqm and includes two cisterns which contain the solution needed by the process, a reactor where the chemical reaction occurs, and a filter which divides the powder from the liquid phase, allowing for treatment in the drier at the end of the process. All this equipment is protected by the Glove Box, a structure which prevents the operators' contact with any of the agents used during the process. The whole plant is monitored by an automated system which simplifies the activities while granting improved safety. The plant's dimensions allow a daily production of approximately 1 kg of CAM which is an amount sufficient to manufacture 50 small batteries. While this plant is mainly dedicated to internal and external testing and evaluation, the LIFE+ GLEE process can be scalable to hundreds of times the size by replicating the process with larger equipment and/or multiple lines.

Pilot Plant: Key Figures

300 sqm

This modern lab, equipped with a reactor that has an innovative layout, is able to simulate real industrial conditions. Its design makes this plant an example of sustainability and safety.

1 kg CAM = -1,1 kg Solvent

The lab produces 1 kg of Cathode Active Material (CAM) per batch, corresponding to 1.1 kg of solvent saved.

PER BATCH

50

Each batch of CAM is equivalent to the production of 50 small phone batteries per day.



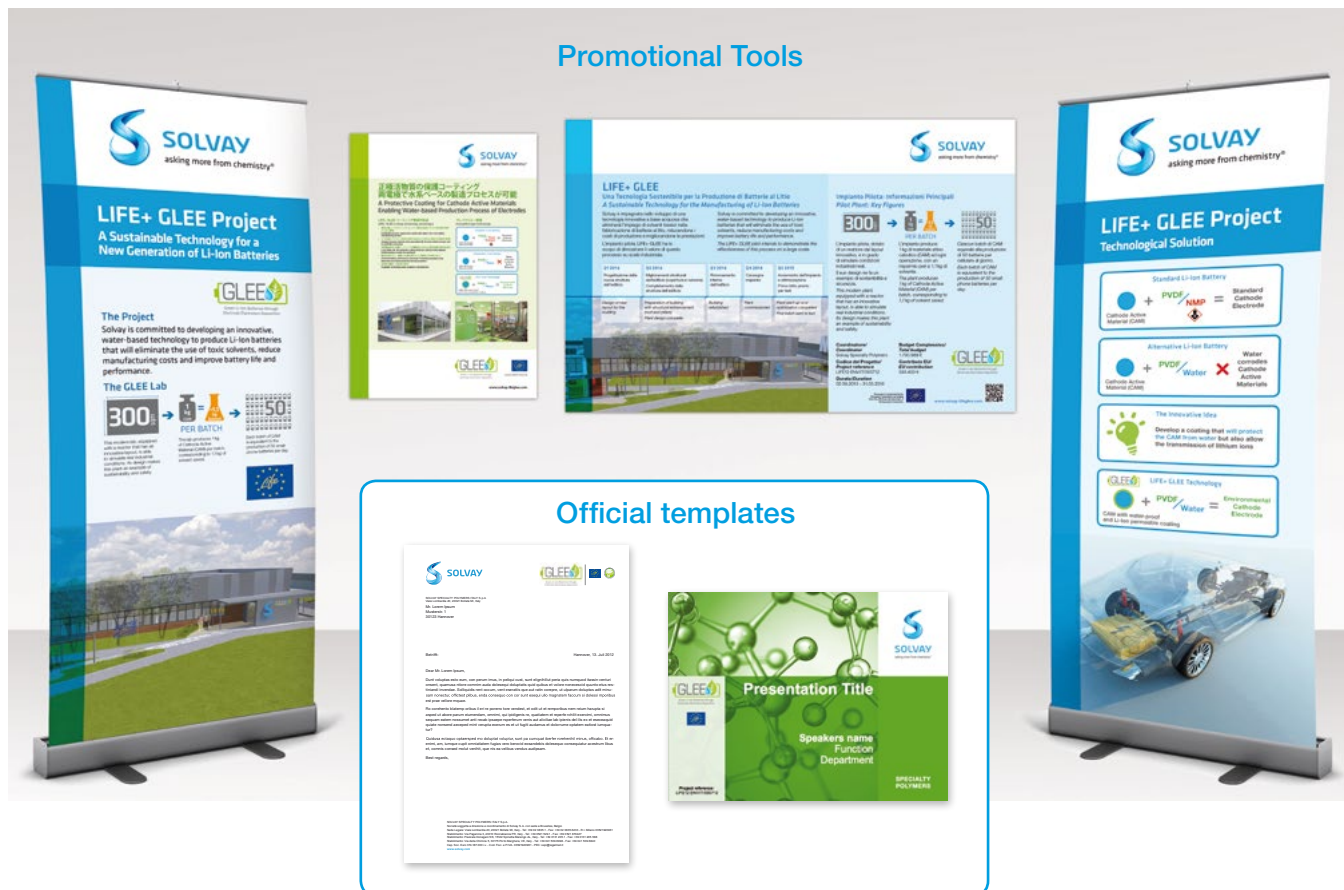
Communication Activities

LIFE+ GLEE utilizes several integrated communication tools and activities to support and promote the project to everyone directly and indirectly involved in its implementation.

These tools include media, internet, informative documentation and events.

Visual identity

Different graphical elements and communication tools define the project's visual identity and are used for both promotional and official activities.



Conferences and Events

Below a list which includes some of the conferences and events during which the LIFE+ GLEE Project has been presented:

- 225th Electrochemical Meeting (ECS meeting)
Orlando (FL), United States of America, May 2014
- 226th Electrochemical Meeting (ECS meeting)
Cancun, Mexico, October 2014
- Fluoropolymer 2014 (ACS Division of Polymer Chemistry)
San Diego (CA), United States of America, October 2014
- Battery Expo
Tokyo, Japan, February 2015

Web

The Group website, www.solvay.com includes a dedicated section which illustrates in detail the project and its objectives. It is possible to review the most recent developments and activities related to the project.

To obtain direct access to the GLEE section, visit www.solvay-lifeglee.com

Glossary

Adsorption

A chemical-physical process that consists in the accumulation of one or more substances on the surface of a solid.

Annealing

A heat treatment that alters the physical and chemical properties of a material. It involves heating a material, maintaining a suitable temperature, and then cooling.

Anode

In a battery, the anode is the negative electrode from which electrons flow out toward the external part of the circuit.

Binder

A binder is a material (usually a polymer) that holds or draws other materials together to form a cohesive whole mechanically, chemically, or as an adhesive.

CAM

A cathode active material is the material that participates in the electrochemical reaction of the battery at the cathode side.

Catalyst

The catalyst increases the rate of a chemical reaction. With a catalyst, reactions occur faster and with less energy.

Cathode

In a battery, the cathode is the positive terminal where the current flows out of the device.

Coating

A coating is a covering that is applied to the surface of an object, usually referred to as the substrate.

Drier

A drier is a thermally insulated chamber used for the heating or drying of a substance.

Electrode

The electrodes of a battery are the two positive (cathode) and negative (anode) terminals.

Electrolyte

An electrolyte is a substance that allows flow of ions from one electrode to the other. In the case of Li-Ion batteries, the electrolyte must permit the motion of Lithium ions during charge and discharge cycles.

Filter

A filter is used for the separation of solids from fluids.

Intercalation and de-intercalation processes

Intercalation is the reversible incorporation of a molecule among other molecules or groups of molecules. The opposite process is called de-intercalation.

Ionic conductivity

The ionic conductivity of an electrolyte solution is a measure of its ability to conduct positive or negative ions.

LIFE

Financial instrument of the European Community dedicated to environment protection.

Metallization

Metallization is the process of covering with a metal layer the surface of an object, usually referred to as the substrate.

NMP

N-Methyl-2-pyrrolidone (NMP) is an organic compound. It is a colorless liquid, although impure samples can appear yellow. It is miscible with water and with most common organic solvents. It is used as a solvent, exploiting its non-volatility and ability to dissolve diverse materials.

Electroless

Electroless plating is an auto-catalytic chemical technique used to deposit a metal (or metal oxide) layer on a solid work piece, such as metal or plastic.

REACH Regulations (EU)

Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) is a European Union regulation dated 18 December 2006. REACH addresses the production and use of chemical substances and their respect impacts on both human health and the environment.

Reactor

In chemical engineering, chemical reactors are vessels designed to contain chemical reactions.



Specialty Polymers

Worldwide Headquarters

SpecialtyPolymers.EMEA@solvay.com

Viale Lombardia, 20
20021 Bollate (MI), Italy

Americas Headquarters

SpecialtyPolymers.Americas@solvay.com

4500 McGinnis Ferry Road
Alpharetta, GA 30005, USA

Asia Headquarters

SpecialtyPolymers.Asia@solvay.com

No.3966 Jindu Road
Shanghai, China 201108

www.solvay.com
www.solvay-lifeglee.com

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