

FLUOROPOLYMERS FOR SUSTAINABLE ENERGY TECHNOLOGIES

Marco Apostolo

Solvay Specialty Polymers, R&D Center

Bollate (MI)

marco.apostolo@solvay.com

Truly innovative and performing sustainable energy technologies require new materials and processes. In this regard, fluoropolymers are very effective because of their outstanding properties. Three examples are described in this paper: (i) transparent and weathering resistant ethylene-chlorotrifluoroethylene copolymers, ECTFE, that can replace glass in PV panel enabling the development of flexible and light solutions; (ii) short side chain perfluorosulphonic acid ionomers that are used to develop proton exchange membranes for fuel cell that outperform any competing material; (iii) a special polyvinylidene fluoride grade, PVDF, that is used as electrode binder to improve the performance of lithium ion batteries. The ECTFE and PVDF polymers shown in this paper are utilized on board of Solar-Impulse, a plane that will go around the world in 2015 only powered by solar light.



The picture shows Solar-Impulse flying over San Francisco bay

Fluoropolimeri per tecnologie energetiche sostenibili

Lo sviluppo di tecnologie energetiche sostenibili è una delle sfide più importanti della società moderna. Per vincere questa sfida l'industria chimica è chiamata a sviluppare nuovi materiali e nuovi processi capaci di rendere pienamente competitive tali tecnologie. In questo articolo sono mostrati tre esempi di polimeri fluorurati sviluppati appositamente per migliorare le prestazioni di alcune tecnologie nell'ambito energetico. Il primo esempio riguarda lo sviluppo di pannelli fotovoltaici flessibili, ottenuti sostituendo il vetro con un film polimerico fluorurato. Il secondo esempio è nell'ambito delle celle a combustibile, il cui cuore tecnologico è costituito da una membrana a scambio protonico perfluorurata. Il terzo, ed ultimo, esempio mostra il miglioramento di durata delle batterie al litio ottenuto grazie ad un polimero fluorurato usato nella stesura degli elettrodi. Alcuni di questi nuovi materiali sono usati a bordo del Solar-Impulse, un aereo in grado di volare alimentato unicamente da energia solare. Il Solar-Impulse, che farà il giro del mondo a fine 2015, è anche il simbolo di un futuro energetico sostenibile basato sull'energia del sole.

Sustainable Energy can be defined as “the provision of energy such that it meets the needs of the present without compromising the ability of future generations to meet their own needs”¹. The United Nations General Assembly declared 2012 as the *International Year of Sustainable Energy for All*². European Union, with the “climate and energy package”, defined a set of binding legislation which aims to achieve ambitious climate and energy targets for 2020³. That witnesses the importance and breadth of this subject all over the globe, today and for the future of mankind. Chemical Industry is playing and will play a key role in this challenge by providing better performing and sustainable products and processes.

In particular, this paper shows some recent advancement in sustainable energy technologies thanks to the development and usage of innovative fluoropolymers. Polymers containing fluorine exploit peculiar properties due to the strength of fluorine-carbon bond: the strongest bond in organic chemistry. High chemical and thermal resistance as well as excellent weathering behavior and outstanding dielectric

properties of fluoropolymers can be directly linked to the atomic properties of fluorine atom⁴. Those and other properties make fluoropolymer particularly suited for several applications in the broad area of sustainable energy technology. In this paper three examples are briefly shown: a weathering resistant fluoropolymer film to replace glass in photovoltaic panels, a perfluorinated ion exchange membrane for fuel cells and a fluoropolymeric binder developed for lithium ion batteries.

Ethylene-chlorotrifluoroethylene copolymer as frontsheet of photovoltaic panels

The generation of electricity by photovoltaic's devices (PV) can be divided into three main categories, based on the semiconductor used for the transformation of the light into electricity: bulk crystalline silicon, thin film technology (amorphous silicon, CIGS - Copper Indium Gallium (di)Selenide or CdTe - Cadmium Telluride), organic photovoltaic. Today, almost 90% of the market is dominated by crystalline silicon PV modules with a total market for new installations of more than 26 GW in 2011.

In a PV panel construction, the outer layer that is in contact with ambient and through which the light pass to reach the PV-active layer is called "frontsheet". Usually it is made of glass. Indeed glass provides the needed transparency and weathering resistance; however, the PV panels thus obtained are rigid and heavy. The replacement of glass with a polymeric film is extremely appealing because it could enable the development of flexible and light panels particularly suited for the building integrated PV concepts⁵.

Halar[®]ECTFE, ethylene chlorotrifluoroethylene is a good candidate for glass replacement as front sheet protection of photovoltaic modules due to its high transmittance in visible range, high stability in UV light, low permeability, and excellent weathering resistance^{6,7}. Another advantage of Halar[®]ECTFE is the tendency to self-clean due to its low surface energy. However, while glass is able to stop UV radiation up to 340 nm, Halar[®]ECTFE is fully transparent to UV. This is a problem for some of the materials in the inner part of the panel, for example the EVA (ethylenevinylacetate) used as encapsulant. Indeed, while fluoropolymers are perfectly stable under UV light, many of the other materials used in a PV panel can not withstand such energetic radiation.

To solve this issue a new Halar[®] ECTFE with special UV scavenger fillers have been recently developed. To demonstrate the effectiveness of this film to protect UV-sensitive materials, the Halar[®] ECTFE film with UV scavengers was laminated on PET and then placed in a QUV test chamber equipped with UV-B lamp centered at 313 nm. Fig. 1 shows the effect of UV light on PET (it becomes yellowish), while the Halar[®]ECTFE film with UV scavengers has been able to effectively protect the PET film underneath and appears almost as transparent and uncolored as the sample before UV test.

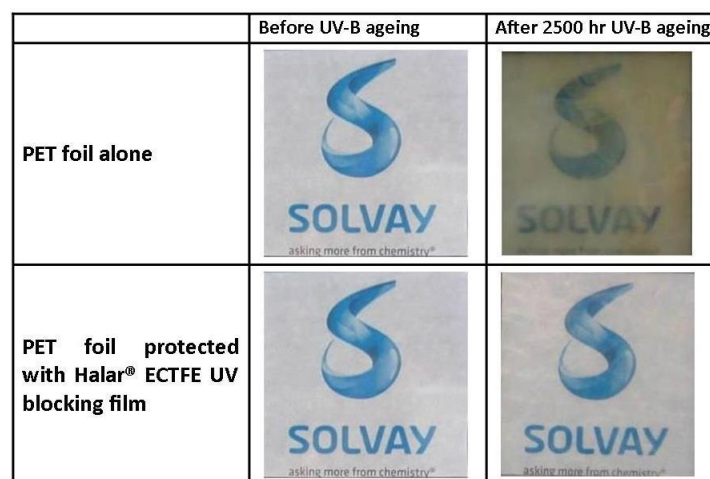


Fig. 1 - PET alone and PET protected by Halar[®] UV blocking after 2,500 hours UV-B ageing (313 nm lamp)

Polyvinylidene fluoride as binder for lithium ion battery electrodes

There are two main factors behind the enormous success of commercialization of lithium batteries. One is related to the continuous evolution of mobile electronic systems such as cellular phones, laptops and tablets, which requires new types of high power and high energy-density batteries. Second, the growing concerns due to CO₂ increasing content in the atmosphere are pushing towards the replacement of

combustion-engine cars with electric or hybrid vehicles. Lithium-ion batteries are the best choice in both cases, because of their high energy density and design flexibility that make these systems outperform the various existing technologies⁸. Today, more than 70% of the market of rechargeable batteries is made of lithium ion batteries, with more than 4,2 M cells sold in 2011 and 9,7 B\$ sales⁹.

In its most common configuration this battery is formed by a graphite anode, a lithium metal oxide cathode (for example, LiCoO_2) and a porous separator soaked with a liquid solution of a lithium salt (typically LiPF_6) in an organic solvent mixture (ethylene carbonate-dimethylcarbonate mixture). Fig. 2 shows a SEM picture of a LiB cross-section with indication of various elements that compose the battery.

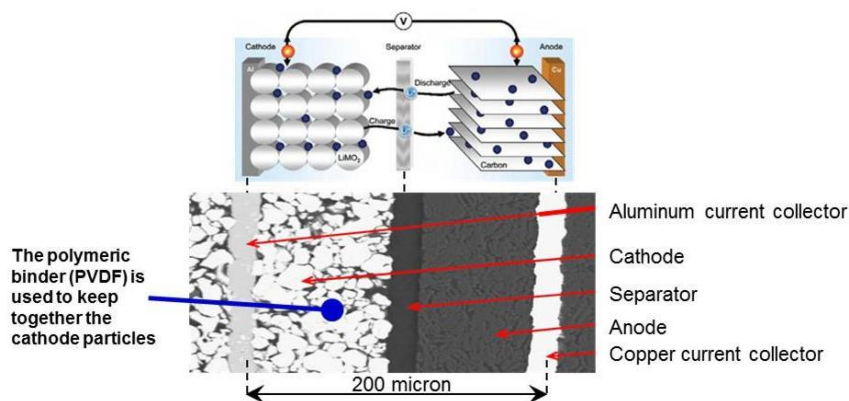


Fig. 2 - Lithium ion battery cross-section (SEM image)

Polymers are widely used in electrode manufacturing as binders, in order to guarantee good adhesion of the electrode to the metal collector and cohesion of active materials particles in the electrodes. These adhesion/cohesion properties are crucial because any detachment inter- or intra-layer would cause a disconnection of the electric conductivity and the stop of the battery electrochemical process. PVDF, polyvinylidenefluoride, is traditionally used as binder because of its excellent electrochemical resistance and binding ability (see Fig. 2). Recently, a new PVDF grade, Solef®5130, that combines the effects of ultra-high molecular weight with the benefit of polar functional groups distributed in the polymer chain, has been developed. The reinforced intermolecular interactions between polymer, active material and metal collector result in increased performances in terms of adhesion (Fig. 3) and chemical resistance in electrolyte. These effects are translated into higher energy density since it is possible to significantly reduce binder content, while the lower internal resistance gives access to higher power density.

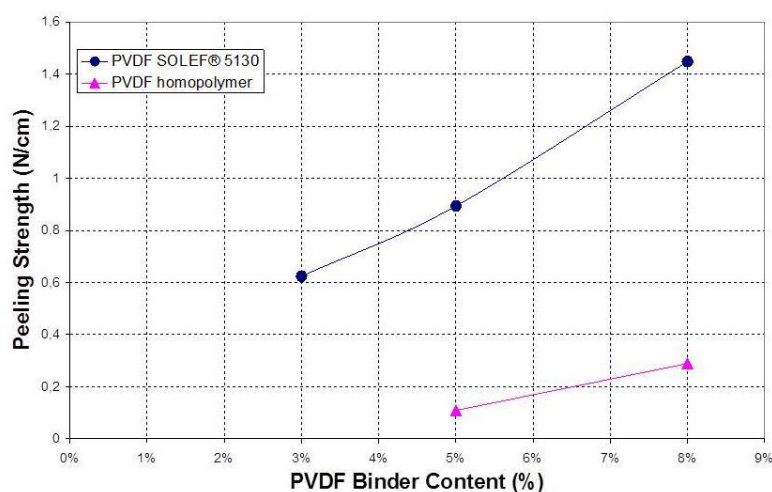


Fig. 3 - Adhesion at cathode with LiFePO_4 active material and different PVDF grades and content

Perfluorosulphonic acid polymer as proton exchange membrane for fuel cell

Polymeric Electrolyte Membrane (PEM) fuel cells¹⁰ are considered today as one of the most promising technologies in the field of renewable power sources and environmentally friendly energy generation, to solve the problems of oil shortage and global warming due to their high efficiency (compared to combustion cycles) and the clean exhausts¹¹. Fuel cells are continuous current generators that operate a combustion process without contacting directly the fuel and the oxidant species, typically producing similar amounts of heat and electric energy.

The most commonly used reagents are air on what is called cathode side (where the reduction of oxygen takes place) and pure hydrogen on anode side (where the hydrogen oxidation takes place); combination of the two generates an operating voltage of 0.5-0.8 volt per cell depending on the operating current value selected. The main product of reaction consists of water that is discharged together with the exhausts, preferentially from the cathode side, where it is formed. The fuel cells are always stacked in electrical series in order to have a generator with a proper voltage; stacks are built with a sequence of 50 to 400 single cells, depending on the application. For some power demanding applications several stacks are connected with each other in order to reach a power size of some hundreds of kW.

Perfluorosulfonic acid ionomers (PFSA) are known since the late Sixties, when the Nafion® ionomers were developed by the Du Pont company and employed as polymer electrolyte in a GE fuel cell designed for NASA spacecraft missions.

In more recent years, the growing interest related to cleaner energy production technologies has promoted the consideration and study of ionomers as proton-exchange membranes (PEMs) in fuel cells. PFSA are generally considered from the scientific community superior to other polymeric ionomers due to their high chemical resistance and high proton conductivity. Again, due to electrochemical stability requirements, perfluorinated materials have been preferred as the best candidates for satisfying the needs of the system. Fig. 4 shows the structure of the most common perfluorinated ionomers available in the literature.

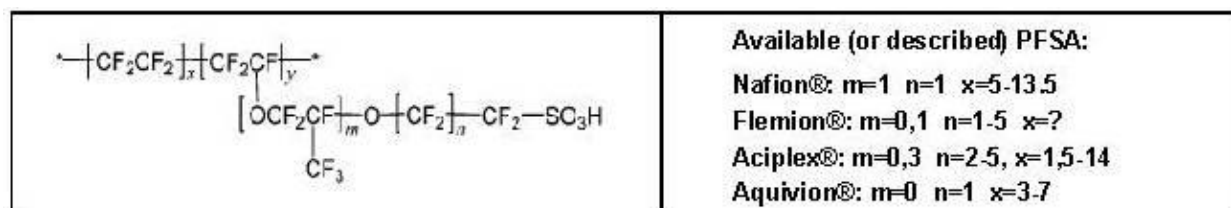


Fig. 4 - Structure of PFSA ionomers

Aquivion® PFSA is particularly interesting because the pendant side-chain which carries the functional ion-transporting group is the shortest of the list, wherefrom this ionomer is known as the short-side-chain (SSC) ionomer. Pretty recent literature shows that proton exchange membranes made with SSC ionomer impart higher power-generating capability in fuel cell^{12,13}. The same ionomer can be used as binder for both fuel cell and electrolysis electrodes. The binder purpose is to keep physical integrity of the catalyst layer and high value of ionic conductivity of the electrode itself. The advantage of perfluorosulfonic materials compared to not-fluorinated competitors can be classified in:

1. superior chemical stability: fuel cell environment is extremely oxidative (especially when reactant humidity is kept low) and peroxide species are frequently detected in both anode and cathode side¹⁴. C-F bond is highly resistant to radical degradation, while the C-H bond is 'easily' degraded;
2. higher ionic conductivity: the sulphonic-acid group has intrinsically a strong acid character, but, because of the electronic attraction favoured by fluorine atoms in the backbone, a stronger acid character is measured when transiting from hydrogenated to fluorinated molecules. The direct consequence of a stronger acidic character is, mainly, higher ionic conductivity, advantage particularly exploited when dry reactants are used. This last feature is illustrated by Fig. 5, where the conductivity of a PFSA is compared to that of an aromatic ionomer as a function of relative humidity.

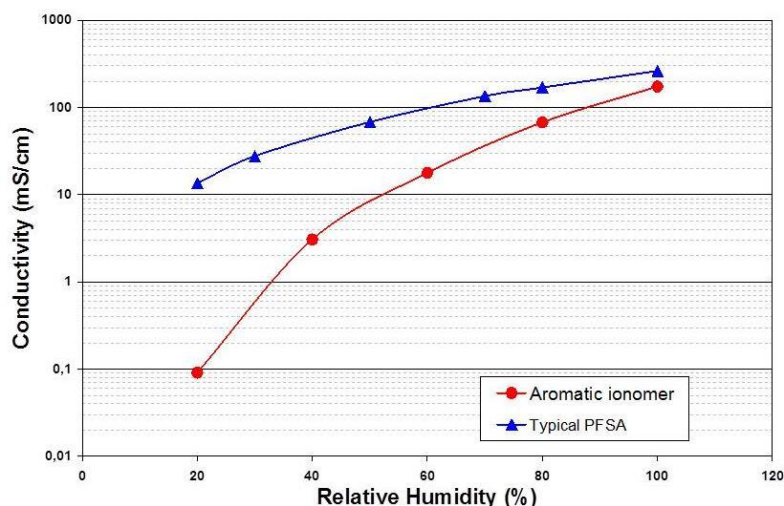


Fig. 5 - Comparison between typical PFSA and hydrocarbon ionomer ionic conductivity as a function of relative humidity

Conclusions

The technologies discussed in this paper are known to be sustainable, meaning that they can provide an energy system based on renewable sources, independent from fossil fuels. However, in a deeper analysis, the sustainability of an energy conversion process should contemplate other aspects, like the lifecycle (eco-profile) of the materials associated with the process, the impact of the required installations (volumetric, environmental), the nature of the energy source and the one of the produced energy. These aspects must be more and more taken into account in order to develop new energy technologies that are fully sustainable, from cradle to grave.

Solar Impulse project, the plane that will go around the world powered by sun only, is a potent symbol of this societal evolution towards an energy system fully sustainable in the long run¹⁵. New materials, like those discussed in this paper are transforming this ideal target into a journey made of real and achievable steps.

References

- ¹Renewable Energy and Efficiency Partnership, Glossary of terms in sustainable energy regulation, 2004, 8.
- ²General Assembly, United Nations General Assembly Resolution A/RES/65/151 16 February 2011, 1-3.
- ³http://ec.europa.eu/clima/policies/package/index_en.htm
- ⁴E. Giannetti, in *Materiali Polimerici Cristallini e Liquido Cristallini*, XXI Convegno-scuola AIM, AIM (Ed.), Pisa, 1999, pag. 333.
- ⁵http://en.wikipedia.org/wiki/Building-integrated_photovoltaics
- ⁶J. Abusleme *et al.*, 23rd EUPVSEC Proc.: 4AV 3 52, Performances of Fluoropolymers in PV-Cells, 2008.
- ⁷G. Wypych, *Handbook of Material Weathering*, 4th Edition, ChemTec Publishing, Toronto, 2008.
- ⁸J.M. Tarascon, M. Armand, *Nature*, 2001, **414**, 359.
- ⁹C. Pillot, The worldwide battery market 2011-2025, BATTERIES 2012, Nice, FRANCE, October 24-26, 2012.
- ¹⁰B. Smith *et al.*, *Journal of Membrane Science*, 2005, **259**, 10.
- ¹¹J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, 2nd Ed., John Wiley & Sons, 2003.
- ¹²A. Ghielmi, *J. of Power Sources*, 2005, **145**(2), 108.
- ¹³V. Arcella *et al.*, *Ind. Eng. Chem. Res.*, 2005, **44**, 7646.
- ¹⁴M. Danilczuk *et al.*, *Macromolecules*, 2010, **43**(7), 3352.
- ¹⁵<http://www.solarimpulse.com/>