AQUIVION™ – The Short-Side-Chain and Low-EW PFSA for Next Generation PEFCs Expands Production and Utilization

Matthias Gebert

This document appeared in

Detlef Stolten, Thomas Grube (Eds.):

18th World Hydrogen Energy Conference 2010 - WHEC 2010

Parallel Sessions Book 1: Fuel Cell Basics / Fuel Infrastructures

Proceedings of the WHEC, May 16.-21. 2010, Essen

Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-1

Institute of Energy Research - Fuel Cells (IEF-3)

Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010

ISBN: 978-3-89336-651-4

AQUIVION™ – The Short-Side-Chain and Low-EW PFSA for Next Generation PEFCs Expands Production and Utilization

Matthias Gebert, Solvay Solexis, Italy

The new Aquivion™ (formerly "Hyflon Ion") ionomer product portfolio of Solvay Solexis is introduced. Both membrane and dispersion grades are presented with some of their properties illustrated by analytical results. In addition to the innovative functional ionomer materials Solvay Solexis also provides a variety of other selected functional materials to the emerging commercial MEA market including inert Galden® heat-transfer fluids, advanced Tecnoflon® high-temperature fluoroelastomers for sealings, aqueous Algoflon® PTFE dispersions or tailored film materials for use as membrane sub-gaskets (membrane rims) which are manufactured to order at small or large scale and are customized in terms of polymer choice, film thickness and geometry.

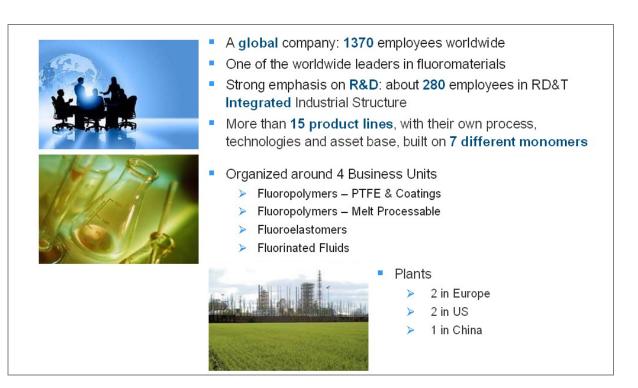


Figure 1: Key data on Solvay Solexis S.p.A. with headquarters in Milan/ Italy.

Figure 1 displays key information of Solvay Solexis, Italian fluoromaterial specialty company and affiliate of the Belgian Solvay Group that emerged from Solvay's acquisition of Ausimont S.p.A. in 2003. Solvay Solexis manufactures on three continents to provide a broad portfolio of fluoromaterials to a variety of industries and applications that demand the superior performance of fluoromaterials.

AQUIVION™ – Progress within PFSA ionomers

Solvay Solexis focuses on the incorporation of a short-side-chain ionomer in their membrane and dispersion products. Shortening the length of the polymer's side chains results in increased mechanical stability of the polymer; confirmed by stress-strain tests or DSC scans [1]. Such Differential Scanning Calorimetry reveals an increased level of crystallinity for shorter pendant group chains when comparing equal equivalents weight (EW) or ion-exchange capacity (IEC), respectively.

AQUIVION™ - What makes the difference

Shifting physical properties of the PFSA material in the right direction can lead to the desirable progress in PEFC optimization. The repeated requests for "high-temperature membranes" that would enable smaller cooling systems, reduced gas humidification and less active area are answered by Aquivion™ through...

- its higher thermal stability thanks to a roughly 40 °C higher softening temperature T_G compared to longer side chains,
- its capability to more strongly absorb and retain cathode product water inside the membrane for self-humidification, and
- its cutting-edge proton conductivity and water mobility levels, especially when operating PEFCs with gases at low relative humidity.

Exploiting the advantages of the short-side-chain structure and reducing the Equivalent Weight to a satisfactory level are the key choices that provide significant performance improvement of the fuel-cell device.

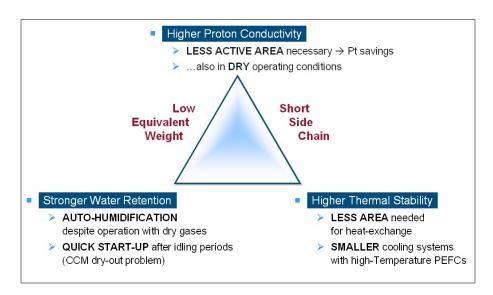


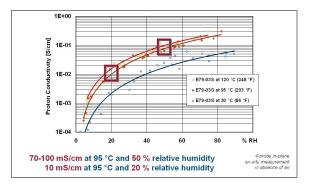
Figure 2: Lower system size and cost via benefits of advanced AQUIVION™ properties.

AQUIVION™ – Exemplified membrane properties

The following three figures describe test results that indicate the physical advantages of Aquivion™ with regard to a high-temperature operation at low reactant pre-humidification.

One exhibits proton conductivity curves of the E79-03S grade at ambient temperature as well as 95 and 120 °C (200 and 250 °F). Even at 95 °C and 20 % rH over 10 mS/cm can be retained as proton conductivity. Absolute values were well reconfirmed by a Round Robin testing within the European Autobrane project (2006-09), see [2] for detailed results of further 12 institutes who screened **Aquivion™ E79-03S** proton conductivity under three pre-defined cell conditions.

The chart on the right illustrates the pronounced effect of superior water retention at 90 °C and quasi dry conditions. Long-side-chain ionomer membranes or baseline Aquivion™ materials such as E87-05S (EW 870, 50 microns) lose cell voltage when lowering reactant pre-humidification. Advanced E79-03S (EW 790, 30 microns) maintain the cell voltage by efficient auto-humidification through absorption and transport of cathode product water.



90 °C - 1.1 bar abs - 50 cm² - 0.6 A/cm²

0.75

0.70

0.70

0.75

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

0.70

Figure 3: AQUIVION™ E79-03S proton conductivity as a function of rH and T (30 μm).

Figure 4: AQUIVION™ E79-03S water retention capability in hot and dry conditions.

The possibility to continuously operate an ionomer membrane at high temperature is limited by its softening temperature. Under fully dry conditions this temperature can be determined as the polymer's alpha-transition peak (for Aquivion™ indicatively between 125 and 140 °C).

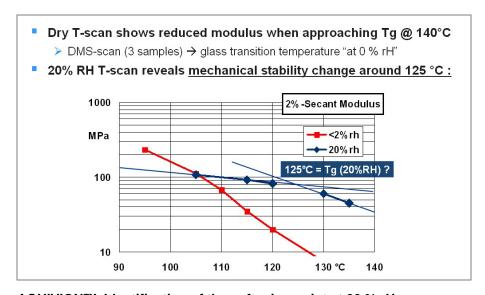


Figure 5: AQUIVION™, Identification of the softening point at 20 % rH.

Validating the situation under partial humidification requires a series of stress-strain tests at fixed rH and various temperatures, as shown by the chart's diamonds. A change in slope of the modulus reduction typically indicates an alternation in the polymer structure; which in case of Aquivion™ can be observed at around 125 °C for measurements at 20 % relative humidity. Lifetime test results are a development criterion of similar importance for the assessment of membrane quality. Solvay Solexis is equipped with several test stations for long-life testing. Selection of suitable combinations of operating conditions and membrane grades will allow simultaneous optimization of both performance and lifetime requirements. More detailed technical discussion of ex-situ and in-situ differences of long- and short-sidechain PFSAs can be found in [3] while [4] and [5] discuss resistance of Aquivion™ against radical attack, again in comparison to LSC PFSAs.

AQUIVION™ – Dispersions

Various grades of Aquivion PFSA ionomer dispersions in different solvent systems do not only provide a powerful raw material for catalyst ink development, but are also essential for other applications such as membrane recasting or treatment of hydrophobic surfaces to impart better water wettability.

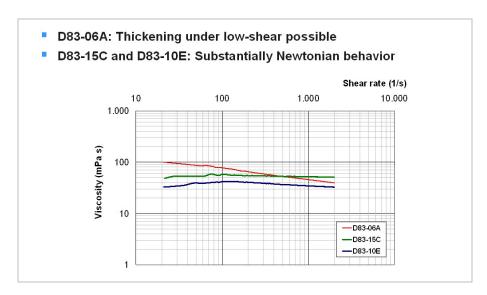


Figure 6: AQUIVION™, Typical rheological curves of various dispersion grades.

Solvent compositions range from predominantly alcoholic (80 % propanol) to virtually aqueous-based. Likewise ionomer concentration can be moderate (6 %) or elevated (20 %). The combination of these two factors – with alcohol acts as a polymer swelling agent – affords different grades with varying rheological behavior, as shown in the graph. Both the absolute viscosity level and its dependency on the shear rate exhibit specific characteristics to adapt the grades to their intended use.

Solvay Solexis supplies all commercial ionomer dispersions worldwide in various containers of 0.5, 5 or 60 liter capacity to both industrial manufacturers and R&D organizations. AQUIVIONTM materials are accessible via **solexis.ionomers@solvay.com**. Small-volume samples are dispatched worldwide by the distributor **Ajedium Films LLC** based in Newark,

Delaware (USA). Industrial customers are supplied directly by Solvay Solexis's customer service center CCS in Milan/Italy.

References

- [1] A. Ghielmi et al. "Proton exchange membranes based on the short-side-chain perfluorinated ionomer", J. Pow. Sourc. 145(2005) 108-115, Fig. 3.
- [2] D. Jones et al. "Progress MEA 2008 : Progress in MEA Components for Medium and High Temperature Polymer Electrolyte Fuel Cells", La Grande Motte, France. September 21-24, 2008. Poster Presentation. (www.progressmea2008.eu)
- [3] L. Merlo et al. "Membrane Electrode Assemblies Based on Hyflon[®] Ion for an Evolving Fuel Cell Technology", Sep. Sci. Techn. 42:13, 2891 2908
- [4] L. Merlo et al. "Resistance to peroxide degradation of Hyflon® Ion membranes", J. Pow. Sourc. 171(2007) 140-147
- [5] S. Schlick et al. "Ranking the Stability of Perfluorinated Membranes Used in Fuel Cells to Attack by Hydroxyl Radicals and the Effect of Ce(III): A Competitive Kinetics Approach Based on Spin Trapping ESR", Macromolecules, 2010, 43 (7), pp 3352–3358