



## Biography of Prof. Alain Tressaud

Prof. Alain Tressaud was educated at University of Bordeaux in Bordeaux, France, where he obtained his Doctorate in Physical Sciences in 1969. His international career began in 1972, when he worked as a NATO Fellow at the University of California, Berkeley under the mentorship of Prof. Neil Barlett. He subsequently became a senior research fellow at CNRS in 1976, and then its CNRS Research Director duties began in 1982 (Emeritus, since 2009). Additionally, he has been an Invited Scientist at: University California, Berkeley (1982), Philipps Universität, Marburg (1982), Kyoto University (1986), Universidad La Laguna, Spain (1991), NPL, New Delhi, (1994), and Aichi Institute Technology, Japan (2000). He was also Invited Professor at Kyoto Univ. for several months in 2009 and is Associate Scientist at Institute Jozef Stefan, Ljubljana, Slovenia since 1998.

He is Fellow of the European Academy of Sciences, Brussels, Belgium since 2007 and served as its President in 2017-18, being now the Vice-President. He is the Founder of CNRS French Network on Fluorine.

Among the many notable breakthroughs achieved by A. Tressaud, the highlights include:

**Discovery of high or unusual oxidation states in d transition elements:**  $\text{Ni}^{3+}$ ,  $\text{Cu}^{3+}$  in cryolite-type phases,  $\text{Co}^{4+}$ ,  $\text{Cu}^{4+}$  in  $\text{K}_2\text{PtCl}_6$ -type compounds can be quoted as examples. In most compounds, the stabilization of the oxidation state could be correlated with factors such as the reticular energy of the involved structure, or the presence of competitive bonding. The investigation of mixed-valence in palladium compounds such as  $\text{Pd}_2\text{F}_6$  yielded an unique increase of electrical conductivity of six powers of ten under pressure : the highest jump ever observed in a fluoride. This phenomenon was attributed to the creation of electronic levels in the band structure resulting from the pressure-induced electronic transition:  $\text{Pd(II)} + \text{Pd(IV)} \rightarrow 2\text{Pd(III)}$ . These discoveries were initiated during the post-doctoral stay of A. Tressaud in 1972 at University of California, Berkeley in Neil Bartlett's laboratory, the great scientist who discovered in 1962 xenon fluorides and subsequently developed noble-gas chemistry. Many of these investigations have been carried out in the scope of a regular cooperation induced by Paul Hagenmuller, at that time Director of LCS, Bordeaux with Neil Bartlett over more than 30 years.

**New series of ferrimagnets and ferromagnets :** Most series of the families of ferrimagnetic and ferromagnetic fluorides have been synthesized and characterized by the Bordeaux' group. Several new types of magnetic materials were prepared in weberites, chiolites, perovskites and derived phases. Among those materials, we can quote the fluorinated compounds exhibiting the highest Curie temperatures ever found for fluorides: the weberite  $\text{Na}_2\text{NiCoF}_7$  for fluoro-ferrimagnets, and  $\text{NiMnF}_6$  for fluoro-ferromagnets. The weakly ferromagnetic  $\text{FeF}_3$ , which is among the rare compounds being both transparent and attracted by a magnet at room temperature was also particularly investigated for its unique magneto-optical applications.

The discovery of these new families of compounds had a decisive impact on other researches carried out by other classes of scientists because they provided :

- solid state physicists with experimental objects allowing them to test theoretical magnetic ordering models,
- crystallographers and solid state chemists with original architectures in which the constituting species could consist in layers, chains, trimers, tetramers, rings, etc.

**Graphite intercalation compounds (GIC) and carbon – fluorine system:** Many papers of A. Tressaud deal with the fundamental aspects of intercalation processes in graphite and in carbonaceous materials. Most behaviors could be elucidated in terms of charge transfer, electronic configuration of guest species, dimensionality of the magnetic interactions. For fluorinated carbon blacks for instance, a two-step mechanism involving carbon either with  $sp^2$  or  $sp^3$  hybridization could be pointed out. The potentialities of such materials have been illustrated by their extremely high conductivity values, i.e. in metal fluorides-GICs or in graphite fibers intercalated by fluorine:  $\sigma (C_{10-14}F) = 4 \times 10^5 \text{ Scm}^{-1}$ , approaching the conductivity of copper for instance. In the domain of energy storage, rf-plasma fluorination of carbon anodes allowed increasing the capacity of Li-ion batteries by more than 15 %. Most investigations have been carried out in the scope of wide international cooperations, in particular with several Japanese groups, e.g. those of Profs. Watanabe, Nakajima and Touhara.

Recent works have illustrated the great interest of nano-sized carbon particles on the performance of Li battery

**Fluorine-induced superconductivity:** The discovery of high-temperature superconducting cuprates in 1986 yielded unprecedented activities in varied scientific fields. In particular it was discovered in 1988 in Bordeaux that the extreme reactivity of  $F_2$  and fluorinated gases could be used with the  $YBa_2Cu_3O_{7-x}$  series to remove impurities from grain boundaries and to protect the material against air moisture; the critical current density  $J_C$  was also notably increased. Some times later, similar  $F_2$  treatments allowed the discovery in Bordeaux of the drastic transformation of the insulating pristine  $La_2CuO_4$  into a superconductor by intercalation of F-species.

Mechanisms of interaction occurring between the reactive species present in  $F_2$  atmosphere or  $CF_4$  rf-plasma and superconducting ceramics were subsequently proposed through detailed X-ray photoelectron spectroscopic analyses.

**Improvement of surface properties of materials** via low-temperature plasma reactions: Using reactions in various fluorinated media, i.e. radio-frequency (rf) cold plasmas or fluorinated gases, the Bordeaux group has been able to drastically modify the surface and interface properties of many classes of materials, such as polymers, metals, semiconductors, carbons and oxide ceramics. The concerned physical properties include electrical conduction, adhesion, permeability, superconductivity, hydrophobicity/wettability balance. For instance, using  $CF_4$  rf-plasmas, the nature of the electronic configuration of the carbon atoms involved in the C-F bonds could be easily tuned from  $sp^2$  to  $sp^3$ . An original two-step fluorination mechanism could be proposed for the fluorination process of carbon blacks. The formation of a fluorine containing insulating layer on the surface of these materials increased the repulsion effect between the nanoparticles, leading thus to an increase of the electrical permittivity. Switchable hydrophobic/hydrophilic porous alumina could be prepared for improved uses in lithographic offset processes (Agfa- Gevaert patent, 2006).

**Bordeaux' multi-functional devices devoted to fluorine chemistry** constitute a unique setting in inorganic chemistry groups worldwide. In these equipments, designed and managed by his co-workers Alain Demourgues and Etienne Durand, most fluorinated reagents can be currently used:  $F_2$ ,  $NF_3$ ,  $ClF_3$ , aHF,  $CF_4$ ,  $XeF_2$  and noble-gas fluorides, in a very wide range of temperatures (up to  $1000^\circ\text{C}$  under aHF) and pressures (up to 500 bar with pure  $F_2$ ), crystal growth under fluorinated atmospheres, radio-frequency plasmas ( $CF_4$ ,  $CHF_3$ ,  $C_3F_8$ , c- $C_4F_8$ ), etc.

In recent years, the interests of A. Tressaud's research group have also been focused on various **mixed-anion compounds**. Among the important achievements, we may point out:

- Synthesis of thermally stable Al and Fe (oxy-)(hydroxyl-)fluorides as catalysts for the synthesis of CFCs substitutes,
- Determination of the electronic transitions at the origin of absorption in the visible range for rare-earth (oxy-)fluorosulfides, and the use of these materials as red or yellow pigments (Rhodia patent),
- New series of (hydroxy-, oxy-)fluorinated UV absorbers for the protection of wood and various materials,
- Chemical storage and secured delivery of fluorine (Comurhex-Areva patent, 2006),
- New carbonaceous nanoparticles as active material in primary lithium batteries,
- Ligand field engineering methodology for new 5d metal ion complexes ( $Os^{4+}$ ,  $Ir^{4+}$ ), featuring extremely strong magnetic anisotropy.

Besides the importance of the results obtained in all above fields at the fundamental level, numerous applications have been found in the scope of collaboration programmes with relevant industries. The following applied fields are concerned: catalysis and fine chemistry / medical techniques and biomaterials / nuclear industry / automotive / wood protection/ microelectronics and optics / energy storage, etc

To date, Prof. Tressaud has authored more than 360 papers in International Journals and 12 international patents. He edited 12 books or volumes of books series. He has organized numerous international meetings, presented more than 65 invited lectures in international symposia, and more than 60 invited seminars in industrial or university centers. His accolades include the *Grand prix CEA de l'Académie des sciences* (2008), "Award for creative work in fluorine chemistry", American Chemical Society (2011), and the *Henri Moissan International award* (2012).

Prof. Tressaud is Member of Société Chimique de France (since 1974; Distinguished Member, 2015), American Chemical Society, Fluorine Division (since 1987), and Fluorine Group of the RSC (since 2002).

Books written/edited by Alain Tressaud:

