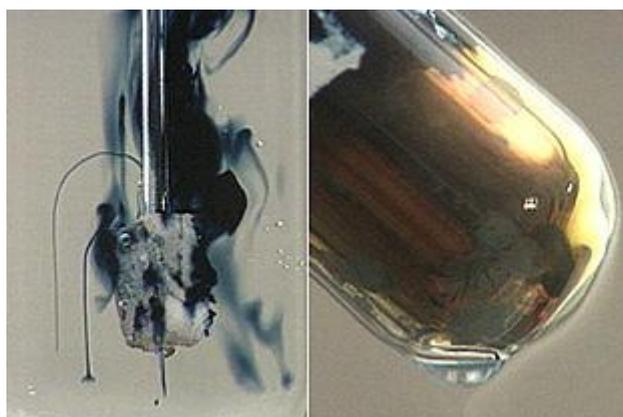


## **‘ELECTRIDES’: ELECTRONS CLAIM THEIR INDEPENDENCE**

*By Dr Antonio Torrisi*

It was about two hundred years ago when Sir Humphrey Davy, a brilliant English scientist and poet whose fame is acknowledged for the discovery of alkaline metals (potassium, sodium, magnesium, barium), observed a surprising phenomenon: potassium metal exposed to ammonia vapours forms gold-blue coloured materials.

About one hundred years later the American chemist Charles Kraus claimed, as possible explanation of this phenomenon, that potassium (K) atoms ionise (lose electrons) in liquid ammonia to form a cation  $K^+$  species, while the freed electrons are solvated (surrounded) by the ammonia ( $NH_3$ ) molecules. Several other alkaline metals such as lithium and sodium show similar behaviour when dissolved in amines and in ether solvents (Figure 1). The two phenomena of ‘electron solvation’ and ‘cation complexation’ linked to Davy’s observation, are behind one of the most investigated and promising fields of chemical and materials science research in the last ten years: ‘*electrides*’.



*Figure 1. Photos of liquid ammonia dissolving sodium metal (left: low  $NH_3$  concentration; right: high  $NH_3$  concentration). Copyright George Lazzen (<http://www.flickr.com/photos/georgelazzenby/118260479/#/>)*

‘Electrides’ are compounds in which some electrons ‘claim their independence’ from their atoms, acting as separated individual entities, or rather, as anions with a mass almost 1,820 times smaller than that of the smallest anion ( $H^-$ ).

In the field of solid state physics, a typical general classification of materials based on electronic properties distinguishes between metals and insulators. Metals are characterised by atoms whose valence electrons (the most external orbiting electrons, within a classical representation of atoms) are completely free to move around the solid like a sort of gas and the metallic atoms are in cationic form ( $A^+$ ). This electron gas makes the metal an electrical conductor. On the other hand, insulators are often characterised by cations and anions kept together by the Coulombic interaction and electrons are strongly bonded to the anions and are not free to delocalise around the solid so that no electrical conductivity is present.

Materials scientists know, though, that all materials present defects at any temperature. These defects can be misalignments of atoms (dislocations) or absences of atoms (vacancies). The latter are very important in inorganic insulators and consist of vacancies of ions. A particular type of defect, which well illustrates the concept of ‘electride’, is called ‘F centre’: it consists of an anion

vacancy which is replaced by one or two electrons within the vacancy (depending on the anion charge). These electrons act as a separate individual entity and behave as anion. The name comes from the German word 'Farben', which means colour. In fact this defect gives origin to colours in gems and other precious stones because the electron in the anion vacancy can undergo energetic excitations which can be promoted by absorbing specific frequencies of visible light (or colour components). As a defect, an 'F centre' is randomly displaced around the solid, without fixed proportions with respect to the other atoms and without regular spatial repetitions of itself in the crystal. An 'electride' can be viewed as a material having 'F centres' in fixed proportion and regular spatial repetitions within its structure. Hence in an 'electride', electrons acting as anions repeat according to the symmetry laws of the crystal and for this reason they can "see" each other and interact with each other in a different way from the way they would behave as defects.

The compounds observed by Davy are closed to the concept of 'electride'. When the alkaline metal enters in contact with the liquid/vapour ammonia, the metal reacts with it, losing an electron. The latter acts as an individual species and  $\text{NH}_3$  molecules start to surround either the metal cations  $\text{A}^+$  ('cation complexation') or the electrons ('electron solvation') and in this way they stabilise the system and prevent the electron and the metal cation meeting each other again and reversing the initial reaction. The only difference from the 'electride' is that the overall system is in a liquid, disordered state. Nevertheless, if the system can be crystallised and build a structural regularity as a crystal, it would become a typical example of an 'electride'.

Davy's compounds are still studied today and in particular  $\text{Li}^+(\text{NH}_3)_4$  material. While in 1968 N. Mammano and T.J. Sienko found that this compound was the lowest melting point metal known, with a crystallisation temperature of  $-184\text{ }^\circ\text{C}$ , in 2011 scientists from Cornell University and State University of New York exploited the far bigger complexity of this compound. Studying the different solid phases of the material at different temperatures and pressures, they found that the highest in temperature (phase I, between  $-191$  and  $-184\text{ }^\circ\text{C}$ ), is a metallic plastic phase, the second intermediate phase (phase II, between  $-248$  and  $-191\text{ }^\circ\text{C}$ ) is less metallic and the latter phase (phase III, below  $-248\text{ }^\circ\text{C}$ ) is insulating with an antiferromagnetic order. In phase I, the term "plastic" relates to the disordered spatial orientation of the  $\text{Li}^+(\text{NH}_3)_4$  species within the crystal lattice, the electrons are nearly free like in a typical metal. In phase II, though, they are much less free and they are mainly located within interstitial regions between  $\text{Li}^+(\text{NH}_3)_4$  ordered species in the crystal lattice. In this case they do behave as proper localised anions and the material is an 'electride'. In very low temperature phase III the interstitial, individual electrons 'see' each other even better and they interact by tuning their intrinsic magnetic moment (spin) in a highly correlated and ordered orientations, one opposite to the other (antiferromagnetic order). The latter property is typical of many 'electrides' at low temperatures.

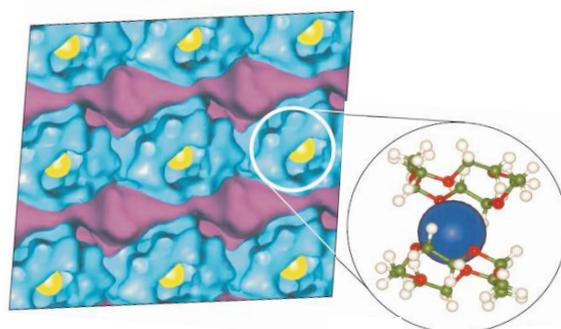


Figure 2. Structure of  $\text{Cs}^+(\text{15-crown-5})_2\text{e}^-$  organic 'electride': independent electrons in the channels are represented in mauve. Organic molecules are in blue and  $\text{Cs}^+$  cations in yellow. Detailed picture of the molecule is given in the inset.

In the last ten years scientists have attempted to synthesise stable organic ‘electrides’, similarly to the progenitor Davy’s compounds. A common feature is the presence of an alkaline metal, because these elements lose their valence electron/electrons quite easily. In order to coordinate alkaline cations in a network structure, scientists have looked for specific organic molecules such as cryptands or crown-ethers with a complex corrugated structure which folds around a sphere and possess ether carbonyl (C=O) groups or nitrogen atoms, both having great affinity for alkaline cations. These molecules, in turn, assemble in a network which leads to the presence of cages and channels in which the dissociated electrons are located, as is illustrated by  $\text{Cs}^+(\text{15-crown-5})_2\text{e}^-$  compound (Figure 2). A big problem with the organic ‘electrides’ is their chemical and thermal instability, which makes them decompose easily at room temperature. Using different strategies (large alkaline elements and appropriated cryptands) assisted by computer simulations, scientists have successfully overcome this problem and synthesised organic ‘electrides’ which are stable up to room temperature.

Another strategy used by scientists for the synthesis of stable ‘electrides’ follows the inorganic route, without the use of chelating organic molecules. Within this route there are various strategies. One of these consists of applying very high pressures to conventional alkaline metals. In 2009 an international collaboration of scientists published in *Nature* a study on metallic sodium becoming transparent and insulating at about 200 GPa (about 2 000 000 times the atmospheric pressure). This surprising phenomenon is due to the compression of valence electron “orbits” (bearing in mind a classical picture of the atoms), which determines a stronger repulsion between electrons, which consequently move apart from the other electrons of the atomic species into the interstices between the atoms: this is a typical imprint of “electrides”. The new location also implies much greater difficulty for the electron to flow around the solid, as it would do in a metal, so that the material becomes electrically insulating. Interestingly, in 2010 scientists from China observed the same behaviour of electrons locating in lattice interstices for magnesium at high pressure (756 GPa), but in this case the “electride” form is still metallic.

Scientists have also turned their attention to another type of material, potentially useful to design “electrides”: zeolites. These are materials based on silicon, aluminium and oxygen interacting species, which are interconnected to generate a porous framework with cages and channels. The framework has an overall negative charge, due to the fact that aluminium cation ( $\text{Al}^{3+}$ ) has a less positive charge than silicon cation ( $\text{Si}^{4+}$ ). The residual negative charge of the framework is balanced by the presence of alkaline cations in the pore. By inserting an excess of alkaline metals into zeolitic pores it is possible to generate clusters of metals and electrons occupying the same space which are similar to “electrides” and they are called “alkalides”. Scientists are even closer to designing proper inorganic “electrides” by using purely silica -silicon and oxygen- based zeolites, in which they can introduce large alkaline atoms such as caesium Cs undergoing oxidation. The resulting  $\text{Cs}^+$  cations reside in the large channels of the zeolites and the stripped electrons are independently located in neighbouring cavities.

Finally, in 2003 the group of Hideo Hosono at Tokyo Institute of Technology fabricated a ceramic material with very peculiar structure based on calcium oxide (CaO) and alumina ( $\text{Al}_2\text{O}_3$ ), which are typical components of cements. The structure (abbreviated with the name C12A7) arises from interconnected small cages similar to those present in zeolites, but much smaller. The cages form a positively charged framework and, in order to guarantee the charge neutrality of the material, extra-framework oxygen anions are trapped within some cages, in a proportion of one to six. These extra-framework oxygens are weakly bonded to the framework and under heating at 700 °C, in presence of calcium or titanium vaporized particles, scientists can extract them, and their departure is replaced by the presence of four electrons, each of them occupying one cage. This process transforms C12A7 into an inorganic “electride” (Figure 3a). The properties of these

electrons are astonishing. They “see” each other and their intrinsic magnetic moments adopt an antiferromagnetic orientation as observed in other “electrides”. Because they are weakly bonded to the framework they can be easily excited either with infrared or UV radiation, so that the material becomes transparent. On the other hand, given the fact that there are still free available non-occupied cages, these electrons have a quite high mobility, so that the “electride” is metallic. Hosono’s group also discovered that C12A7 “electride” becomes superconductive (zero effective resistivity) at very low temperature (-272.6 °C). Moreover, this structure is thermally very stable and for this reason can find immediate technological applications.

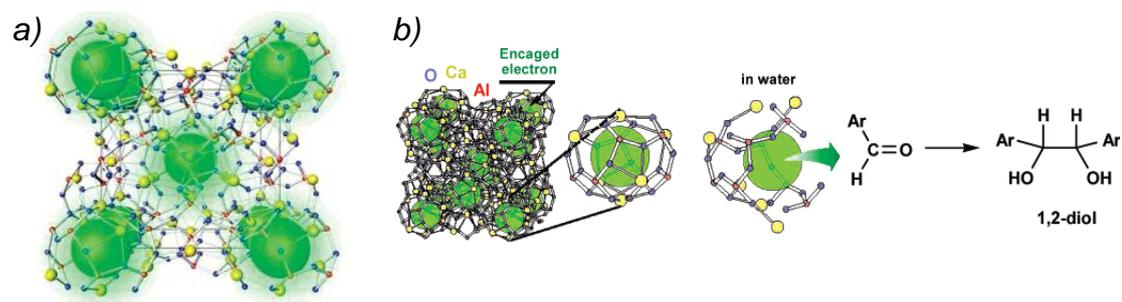


Figure 3. (a) Structure of C12A7 “electride”: electrons in the cages are illustrated by green spherical clouds. (b) Illustrative mechanism of the chemical pinacol coupling reaction promoted by C12A7 “electride” in water.

Indeed, why are “electrides” important and which technological applications are they suitable for? The independent, weakly bound electrons acting as anions within cages or interstices of the crystal structure have a low work function. In virtue of this property they can be easily stripped out of their locations by applying electric fields, making “electrides” very promising materials for thermionic power generation and refrigeration. C12A7 material is already finding application in the production of third generation Light Emitting Diodes (LEDs). On the other hand, the electrons in “electrides” can have a higher mobility, which make them materials with good metallic conductivity. Additionally, with a careful planned design of organic ligands and the right choice of alkaline metals, scientists can fabricate organic “electrides” with a very high hyperpolarizability, which is a fundamental characteristic of high-performance non linear optical materials for optical applications. Last but not least, electrons in “electrides” are chemically reactive and strongly reducing species and they can promote important chemical reactions. Hosono’s group demonstrated that C12A7 “electride” is an efficient solid state reagent in promoting the chemical reduction of organic molecules such as pinacol coupling in water (Figure 3b). This reaction is in general very difficult to initiate and C12A7 “electride” represents a cheap and environmentally friendly optimal reagent. More recently, Hosono’s group and Peter Sushko’s group at UCL have been exploring the possibility to employ C12A7 “electride” surfaces for carbon dioxide reduction and activation.

© Antonio Torrisi, 2011  
Post-Doctorate Research Associate  
Physics & Astronomy Department

## References

- Dye, 'Electrons as Anions', *Science*, 301 (2002): 607-608
- Dye, 'Electrides: Early Examples of Quantum Confinement', *Account of Chemical Research*, 42 (2009): 1564-1572
- Zurek, Wen, Hoffmann, '(Barely) Solid  $\text{Li}(\text{NH}_3)_4$ : The Electronics of an Expanded Metal', *Journal of the American Chemical Society* 133 (2011): 3535-3547
- Redko, Jackson, Huang, Dye, 'Design and Synthesis of Thermally Stable Organic Electrides', *Journal of the American Chemical Society*, 127 (2005): 12416-12422
- Ma, Eremets, Oragnov, Xie, Trojan, Medvedev, Lyakhov, Valle, Prakapenka, 'Transparent dense sodium', *Nature*, 458 (2009): 182-184
- Li, Gao, Wang, Ma, 'Crystal Structures and Exotic Behaviour of Magnesium under Pressure', *Journal of Physical Chemistry C*, 114 (2010): 21745-21749
- Li, Yang, Hou, Zhu, 'Inorganic Electride: Theoretical Study on Structural Electronic Properties', *Journal of the American Chemical Society*, 125 (2003): 6050-6051
- Matsuishi, Toda, Miyakawa, Hayashi, Kamiya, Hirano, Tanaka, Hosono, 'High-Density Electron Anions in a Nanoporous Single Crystal  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4e^-)$ ', *Science*, 301 (2003): 626-629
- Kim, Matsuishi, Nomura, Kubota, Takata, Hayashi, Kamiya, Hirano, Hosono, 'Metallic State in a Lime-Alumina Compound with Nanoporous Structure', *Nano Letters*, 7 (2007): 1138-1143
- Miyakawa, Kim, Hirano, Kohama, Kawaji, Atake, Ikegami, Kono, Hosono, 'Superconductivity in an Inorganic Electride  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3:e^-$ ', *Journal of the American Chemical Society*, 129 (2007): 7270-7271
- Xu, Sun, Muhammad, Su, 'Three-propeller-blade-shaped electride: remarkable alkali-metal-doped effect on the first hyperpolarizability', *Theoretical Chemical Accounts*, 128 (2010): 241-248
- Buchammagari, Toda, Hirano, Hosono, Takeuchi, Osakada, 'Room Temperature-Stable Electride as a Synthetic Organic Reagent: Application to Pinacol Coupling Reaction in Aqueous Media', *Organic Letters*, 9 (2007): 4287-4289