

CHEMISTRY

Electrons in Cement

Peter P. Edwards

A free or ionized electron introduced into a polar molecular solvent such as water or ammonia can be stabilized or trapped by reorientation of the host solvent molecules, leading to the appearance of “solvated” electrons in the liquid (1, 2). For example, in solutions of alkali metals in liquid ammonia, alkali valence electrons are spontaneously ionized by the dissolving metal and released directly into solution. These systems, first described by Sir Humphry Davy in 1808 (3), are brilliant blue, electrolytic conductors when dilute in metal and spectacular golden-bronze and genuinely metallic in concentrated solutions. Kraus, as early as 1914, described the negative carrier of electric current in dilute metal-ammonia solutions as “the negative electron surrounded with an envelope of solvent molecules” (see the figure, panel A) (4). Two years later, Gibson and Argo (5) introduced the term “solvated electrons” to describe this, the simplest anion in solution. On page 71 of this issue, Kim *et al.* (6) report the synthesis and properties of solvated electrons in an entirely new and highly unusual host solvent—cement. The authors have succeeded in preparing solvated electrons in a high-temperature (1873 K) melt of mayenite, $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (abbreviated to C12A7), a component of alumina cement.

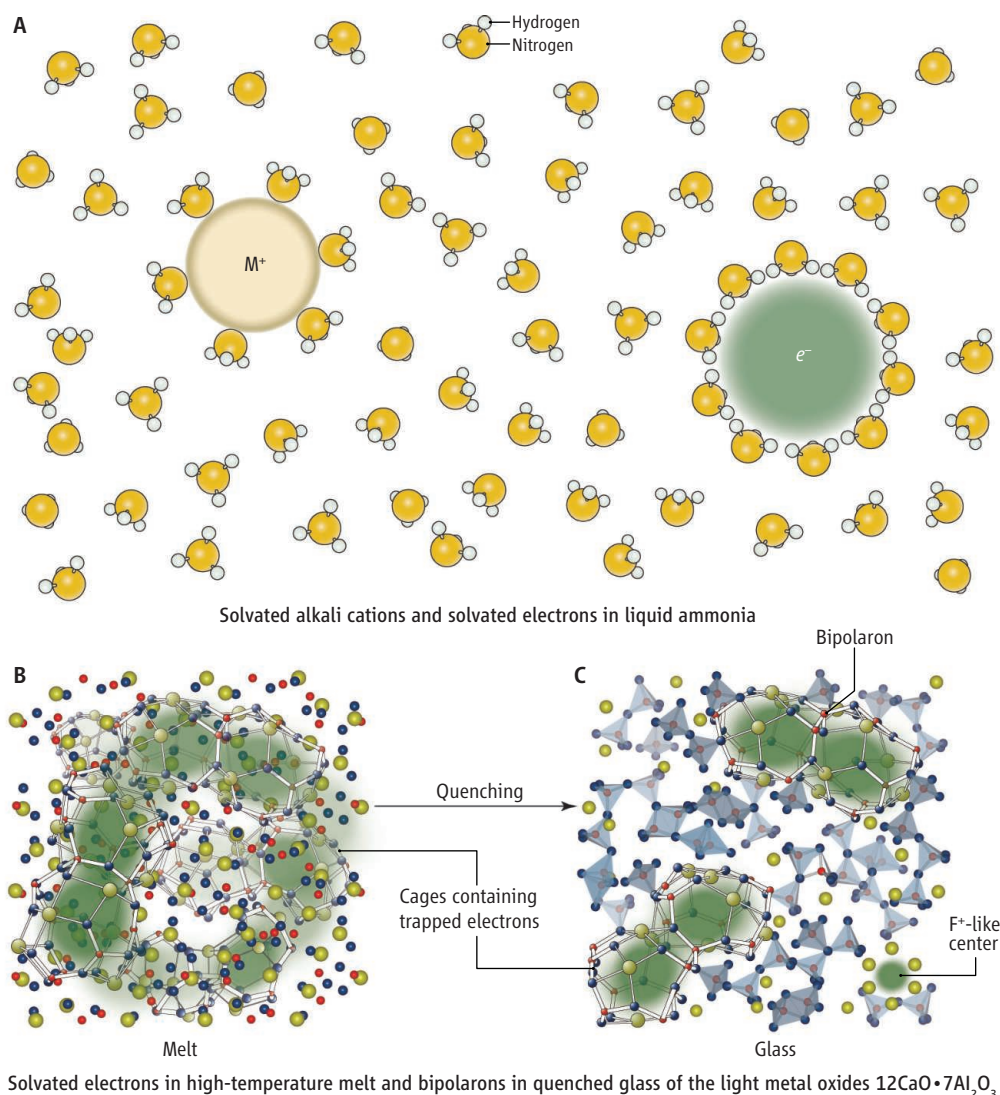
The host material itself is a constituent of slag as a vitreous by-product of the iron smelting process. These stable and recalcitrant light metal oxides are prototype insulators. Therefore, the melt of C12A7 contains no free electrons to carry electric current. On the basis of their earlier single-crystal studies of electron-doped mayenite (7), best considered from a chemical standpoint

as one class of electrides (8), Kim *et al.* wanted to find out whether excess electrons could be introduced and then stabilized as solvated electrons in high-temperature melts of these refractory oxides.

But how can one introduce or dope additional electrons into such unreactive metal oxides so as to turn such a stubbornly resistive insulating material into a conductor of electricity? The innovation reported by Kim *et al.* involves partially replacing mobile oxide ions found in the mayenite lattice by electrons through a high-temperature chemi-

A system of stabilized solvated electrons has been realized in a new type of inorganic electride.

cal reduction with elemental titanium. The introduced electrons are then trapped at oxygen ion vacancies in the melt through solvation (coordination) by calcium ions within the cage structure of the refractory oxide as so-called F^+ -like centers (see the figure, panel B). The transparent, insulating host oxide melt is thereby transformed into a highly colored, electron-doped conducting liquid (abbreviated to C12A7: e^-). Furthermore, the solvated electrons survive, and indeed thrive, in these high-temperature metal oxide electride melts at temperatures up to 1873 K.



Conduction setting in. Models of solvated electrons in (A) alkali metal–ammonia solution [Adapted from (12)], (B) C12A7: e^- melt, and (C) C12A7: e^- glass.

Department of Chemistry, Oxford University, South Parks Road, Oxford OX1 3QR, UK. E-mail: peter.edwards@chem.ox.ac.uk

The three-dimensional connected cages of mayenite and these anionic electrons result in a partially filled conduction band constructed from the accessible, unoccupied orbitals of the cage atoms. Kim *et al.* observed a fundamental change in electrical conduction behavior of the electrified melt as the concentration of introduced electrons increases, from that of (thermally activated) electron hopping between centers to recognizable metallic conduction. Above a critical concentration of solvated electrons ($\sim 10^{21}$ electrons/cm³), there is a transition to a highly conducting, genuinely metallic form of liquid cement. This must surely be one of the most unusual and spectacular observations of the transition to the metallic state (9)—turning liquid cement into liquid metal. The characteristic metallic conduction properties then require the extensive delocalization or percolation of the solvated electron wave functions over the entire melt (see the figure, panel B).

This new design concept of doping high densities of electron carriers into insulating light metal oxides has one further, fascinating twist. The rapid quenching of the high-temperature melt leads to C12A7:e⁻ glassy

materials, but here the overwhelming majority (>99%) of the introduced electrons now exist as a diamagnetic (two-electron) spin-paired state. Kim *et al.* speculate that two individual trapped electron states combine to form a peanut-shaped bipolaronic center (see the figure, panel C), again reminiscent of the situation in alkali metal–ammonia solutions (10, 11). In addition, careful studies of the melting process reveal that the glass transition temperature for the highly conducting C12A7:e⁻ electrified melt is ~ 160 K lower than that for the parent C12A7 glass. This difference means that the network structure of the electrified glass is fundamentally different from that of the parent cement glass, as reflected in the structural model for the melt and glass of C12A7:e⁻ electrified (see the figure, panels B and C).

These important advances open the door for new applications for such robust metallic melts and slags and electronically tunable light–metal oxide glasses. In the area of quantum confinement, the work by Kim *et al.* represents a material showing the ultimate confinement of a quantum particle—an electron “set” in cement. Finally, the word “cement” can be traced back to

Roman times where the term “opus caementicium” described the use of burnt lime as a binder with, for example, volcanic ash to produce pure, natural Pozzolan cement. The advance reported by Kim *et al.* binds the quantum physics of excess electrons, correlated electrons, the metal–insulator transition, and the glass transition with the chemistry and engineering of cement. What a natural combination!

References

1. K. R. Siefertmann, B. Abel, *Angew. Chem. Int. Ed.* **50**, 5264 (2011).
2. J. C. Thompson, *Electrons in Liquid Ammonia* (Oxford Univ. Press, Oxford, 1976).
3. P. P. Edwards, *Adv. Inorg. Chem. Radiochem.* **25**, 135 (1982).
4. C. A. Kraus, *J. Am. Chem. Soc.* **36**, 864 (1914).
5. G. E. Gibson, W. L. Argo, *Phys. Rev.* **7**, 33 (1916).
6. S. W. Kim, T. Shimoyama, H. Hosono, *Science* **333**, 71 (2011).
7. S. Matsuishi *et al.*, *Science* **301**, 626 (2003).
8. J. L. Dye, *Acc. Chem. Res.* **42**, 1564 (2009).
9. P. P. Edwards, C. N. R. Rao, Eds., *The Metal–Nonmetal Transition Revisited* (Taylor & Francis, London, 1995).
10. Z. Deng, M. L. Klein, G. J. Martyna, *J. Chem. Soc., Faraday Trans.* **90**, 2009 (1994).
11. E. Zurek, P. P. Edwards, R. Hoffmann, *Angew. Chem. Int. Ed.* **48**, 8198 (2009).
12. J. L. Dye, *Sci. Am.* **237**, 92 (July 1977).

10.1126/science.1207837

CELL BIOLOGY

Protease Sets Site-1 on Lysosomes

Jin Ye

One of the defining features of how animal cells maintain cholesterol homeostasis is the complex signaling mechanism that releases transcription factors called sterol regulatory element-binding proteins (SREBPs) from their membrane-bound precursors through proteolysis to control the expression of key metabolic enzymes. One of the proteases that catalyze the cleavage is site-1 protease (S1P), a serine protease that is itself membrane bound. One curious phenotype of cultured mammalian cells lacking S1P has been a defect in lysosomes—instead of being targeted to the organelle, certain lysosomal enzymes are secreted out of the cells. On page 87 of this issue, Marschner *et al.* (1) provide one possible explanation—S1P is required for the biogenesis of lysosomes. The authors show that the protease cleaves a precursor

form of *N*-acetylglucosamine (GlcNAc)-1-phosphotransferase, an enzyme that catalyzes an essential step in forming the mannose 6-phosphate signal that targets many enzymes to lysosomes.

Together with site-2 protease (S2P), a metalloprotease embedded in the Golgi membrane, S1P plays a crucial role in regulating cholesterol metabolism through proteolytic activation of SREBPs (2). When cells are overloaded with cholesterol, SREBP is trapped in the endoplasmic reticulum (ER), preventing its cleavage. Upon cholesterol deprivation, SREBP is transported to the Golgi, where S1P catalyzes the first cleavage in the luminal domain. This allows the membrane-bound amino-terminal fragment of SREBP to be cleaved by S2P in the plane of the membrane (see the figure). The second cleavage releases the amino-terminal domain of SREBP from membranes, allowing it to enter the nucleus where it activates genes required for cholesterol biosynthesis and uptake, thereby

restoring cholesterol homeostasis (3). Because of its role in controlling cholesterol synthesis, S1P has been considered a drug target for treating hypercholesterolemia.

Proteolytic activation of SREBPs provides the first example of a signal transduction pathway called regulated intramembrane proteolysis (4). In addition to SREBPs, S1P and S2P also catalyze regulated intramembrane proteolysis of other mammalian transcription factors in diverse conditions. These proteins include activating transcription factor 6 (ATF6), cAMP response element-binding protein 3-like 1 (CREB3L1, also called OASIS), and CREB3L2 (also called BBF2H7). ATF6 is sequentially cleaved by S1P and S2P in cells in which unfolded proteins accumulate in the ER (5). After cleavage, the amino-terminal domain activates the transcription of genes encoding chaperones that assist the folding of ER proteins, thereby allowing cells to survive ER stress. CREB3L1 and CREB3L2 are involved in bone development. The former

Department of Molecular Genetics, University of Texas Southwestern Medical Center, Dallas, TX 75390, USA. E-mail: jin.ye@utsouthwestern.edu

Electrons in Cement

Peter P. Edwards

Science **333** (6038), 49-50.
DOI: 10.1126/science.1207837

ARTICLE TOOLS

<http://science.sciencemag.org/content/333/6038/49>

RELATED CONTENT

<http://science.sciencemag.org/content/sci/333/6038/71.full>

REFERENCES

This article cites 38 articles, 7 of which you can access for free
<http://science.sciencemag.org/content/333/6038/49#BIBL>

PERMISSIONS

<http://www.sciencemag.org/help/reprints-and-permissions>

Use of this article is subject to the [Terms of Service](#)

Science (print ISSN 0036-8075; online ISSN 1095-9203) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. 2017 © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. The title *Science* is a registered trademark of AAAS.