Satisfying metals' thirst vital for high-capacity batteries

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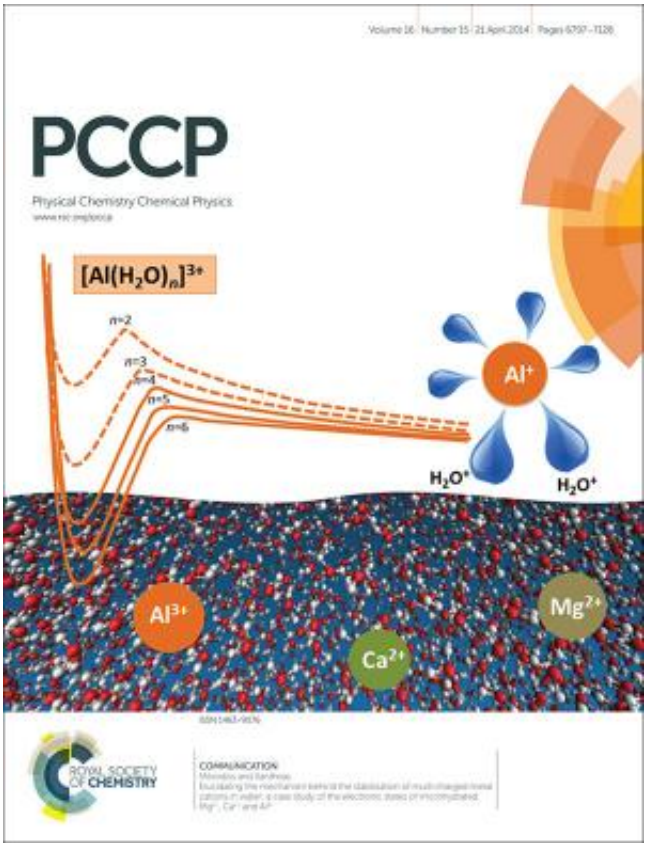

This research graced the cover of *Physical Chemistry Chemical Physics*.

(Phys.org) —When a multiply charged aluminum or magnesium cation encounters a single water molecule, the result can be explosive. The metal ion rips an electron from the water molecule, causing a molecular-level explosion, triggered by the Coulombic repulsion of the two positive

charges on each fragment. But multiply charged metal ions exist in water in countless ways, such as the calcium ions in your chocolate milkshake. At Pacific Northwest National Laboratory, scientists determined the paths that lead to either the hydrolysis of water or the creation of stable metal ion clusters peaceably surrounded by water. It comes down to the pH of the solution, the number of water molecules nearby and the energy needed to remove electrons from the metal, known as the ionization potential.

This research was featured on the cover of a recent issue of *Physical Chemistry Chemical Physics* and in a special issue of Theoretical Chemistry Accounts dedicated to Prof. Thomas H. Dunning, Jr. on the occasion of his 70th birthday.

"This paper describes an elegant use of computational modeling to understand a phenomena that is of fundamental importance in chemistry, yet has many practical applications as well," said Dunning, co-director of the Northwest Institute for Advanced Computing, operated by PNNL and the University of Washington.

Imagine a cell phone battery that lasted for a whole week on a single charge. A car battery that worked for months between charges. A massive battery that stores the intermittent electricity from wind turbines and releases it when needed. In all three cases, today's batteries simply do not hold enough charge. Replacing lithium, which is in the +1 oxidation state, with other metals with multiple charges could greatly increase battery capacity. A roadblock to this future is understanding how to keep multiply charged ions stable.

"We want to use other metals that have +2 or +3 oxidation states," said Dr. Sotiris Xantheas, who led the research at PNNL. "This would double or triple the amount of charge that could be stored in a battery, but before this study, we had no insights on how the ions are either stabilized

or destablizied when their local environment changes."

Numerous experiments show that multiple charged metal ions can generate hydrolysis products through the hydrolysis channel or metal-water clusters through the association channel, depending on the pH. Experiments, however, could not delve into "why" the different products appeared. Using accurate computational models, Xantheas and Dr. Evangelos Miliordos calculated the different electronic states corresponding to those different channels for three metal ions with several water molecules in the gas phase. The ions were Al^{+3}, Ca^{+2}, and Mg^{+2}.

To accurately calculate the location and behavior of the electrons on these metal cation - water clusters, the scientists computed all the states that led to the different channels. The hydrolysis channels, seen at low pH, were also computed for the alkaline earth dication (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) microsolvated clusters.

The team found that each of the various metal ions require different numbers of water molecules to be stable as a microsolvated cluster. For example, the magnesium ion requires at least two water molecules for stability. For aluminum, four water molecules are needed. This stability is due to complex interactions between the ions and the water. The water cluster has an effective ionization potential; that is, the energy needed to pull an electron from a water cluster. The ionization potential increases as more water molecules are added. Eventually, at the right number of water molecules, the ionization potential of the water cluster gets larger than the corresponding ionization potential of the metal, preventing the removal of electrons from the water and creating stability for the metal-water cluster.

While these calculations required extensive computing time, the challenge is the analysis. Both scientists spent considerable time

analyzing and refining the calculations. "A lot of analysis is required to decide what the next step is. At every step you need to decide what the next step is in the process. What did you learn and where do you want to go?" said Miliordos, a postdoctoral fellow from the University of Athens who is working with Xantheas.

The researchers are now working to extend their computational protocol to the solution phase and at interfaces. Extending the methodology will allow the team to better understand the dynamic interactions occurring, eventually leading to better battery technologies.

More information: Miliordos, E, and SS Xantheas. 2014. "Elucidating the Mechanism Behind the Stabilization of Multi-Charged Metal Cations in Water: A Case Study of the Electronic States of Microhydrated Mg2+, Ca2+ and Al3+." *Physical Chemistry Chemical Physics* 16:6886-6892. DOI: 10.1039/C3CP53636J

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