Electronic entropy enhances water splitting

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Credit: George Hodan/public domain

Researchers have long known that cerium is the best element to use when splitting water into hydrogen and oxygen—a key technique in creating hydrogen gas for fuel. But why, exactly, cerium is so successful has been far less understood.

Now a Northwestern University team led by Chris Wolverton has discovered that cerium's electronic entropy, which is created when an electron transitions among various states within an electron shell, is the underlying reason for its success. This finding could help researchers better exploit cerium's entropy for water-splitting technologies.

"In order for water splitting to be fast enough to be practical, you need a large amount of entropy," said Wolverton, professor of materials science and engineering in Northwestern's McCormick School of Engineering. "It turns out that cerium is magic for entropy."

Supported by the US Department of Energy, the research was recently published in *Nature Communications*. Shahab Naghavi, a postdoctoral fellow in the Wolverton Research Group, served as the paper's first author.

Since the 1970s, researchers have touted the potential of a "hydrogen economy," in which hydrogen would replace gasoline to fuel ground transportation. When burned, hydrogen's only byproduct is water, making it environmentally cleaner and more energy efficient than its fossil-fuel alternatives. Pure hydrogen gas, however, is very rare within the Earth's atmosphere.

"The problem is: how do you get the hydrogen in the first place?" Wolverton asked. "Currently, you have to burn hydrocarbons, but that produces carbon dioxide."

Water (or steam) splitting could cleanly and efficiently produce enough pure hydrogen to make the hydrogen economy a true possibility. To split hydrogen from oxygen, researchers use heat generated by solar radiation and cerium oxide, or ceria. Using sunlight to heat ceria to 1,000- to 1,500-degrees Celsius drives a series of reactions that cause hydrogen to split off.

Wolverton and others previously knew that entropy was key to making this reaction possible, but they were unable to find the source of cerium's entropy. "Most people thought entropy was caused by mixing oxygen or vibrations from the heat," Wolverton said. "But we found that it's a different source, and it's not what you might think."

In order for the chemical reaction that drives water splitting to be successful, cerium in the oxide must gain an electron. And that single electron gives rise to whole lot of entropy.

"If there are multiple places for the electron, that gives rise to electronic entropy," Wolverton explained. "The electron can transition from one state to another to another and creates disorder on the electronic scale, and hence, entropy."

Cerium's family of elements—known as rare earths—naturally have more electron states around which the electron can move. Wolverton's team computed the electronic entropy of all 17 rare earths and discovered that cerium demonstrated the largest amount.

"For a long time, we've known that cerium is good for water splitting, but we didn't quite know why," Wolverton said. "Now we partially know why, and that opens up possibilities for future work."

More information: S. Shahab Naghavi et al. Giant onsite electronic entropy enhances the performance of ceria for water splitting, *Nature Communications* (2017). DOI: 10.1038/s41467-017-00381-2

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