Mechanism for formation of aluminum passivation layer

A better understanding of this phenomenon may eventually lead to more effective ways to protect aluminum at pH values above 9.0.

By Dr. Neil Canter
Contributing Editor

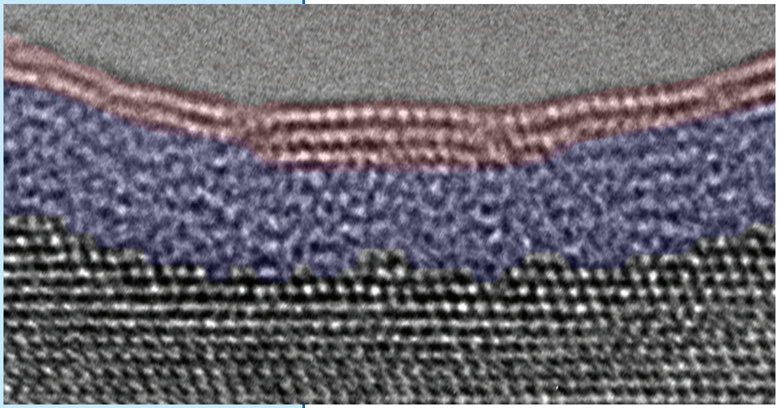


Figure 1. **Passivation of an aluminum metal surface (grey layer) occurs with a bilayer oxide coating of amorphous aluminum oxide (blue layer), and crystalline aluminum hydroxide (red layer).** *Figure courtesy of Binghamton University—State University of New York at Binghamton.*

HIGHLIGHTS

Passivation of an aluminum metal surface initially leads to the formation of an aluminum hydroxide crystalline nature.

Introduction of more water vapor generates a bilayer oxide film with an amorphous aluminum oxide layer displacing the crystalline aluminum hydroxide near the metal surface.

The reason the inner oxide layer is amorphous is because this layer is thermodynamically favored, and the interface with the metal surface and the top aluminum hydroxide crystalline layer is energetically more favorable.

The growing use of aluminum in industrial and automotive applications is increasing as end-users take advantage of the metal's light weight, which leads to improvements in efficiency. Aluminum forms a protective oxide coating that is stable up to pH values of 9.0. Above that pH, the coating dissipates leaving the metal surface vulnerable to corrosion.

But machining aluminum alloys with water dilutable metalworking fluids leads to staining as the metal can turn white, black and gray. Metalworking fluids are formulated to perform at a pH of 9.0 and do include additives known as metal deactivators that can protect against aluminum staining.

A past TLT article[1] discusses a study conducted to better understand how a specific aluminum alloy undergoes surface oxidation. The nickel-aluminum alloy examined has a stepped surface structure that contains a series of terraces or levels that are connected by single atom steps. Exposure to oxygen led to the formation of aluminum oxide stripes that grow on the terraces. Nickel atoms that are not vulnerable to oxidation diffuse into the bulk. As the oxide stripes continue to grow, the terraces bunch together eventually slowing and then stopping the oxidation process.

One of the authors of the past study, Guangwen Zhou, professor of mechanical engineering in the Thomas J. Watson College of Engineering and Applied Science at Binghamton University—State University of New York in Binghamton, N.Y., is working with colleagues to better understand how water interacts with aluminum at the atomic level to form a passivation layer. He says, "Surface chemical processes such as corrosion occur when water interacts with solids such as aluminum. Past studies have been limited in just demonstrating the reaction of water with small lengths of metal surfaces at cryogenic temperatures. But this approach does not provide insight on what occurs under technologically relevant operating conditions."

The opportunity for evaluating how aluminum reacts with water under ambient conditions is now possible through the use of aberration-corrected environmental transmission electron microscopy (ETEM). Zhou says, "This technique allows for the very high-resolution analysis of gas-surface reactions under ambient conditions. Transmission electron microscopy (TEM) is typically vacuum based. ETEM has the capability to differentially maintain a gas phase in the sample area. This allows for imaging of gas chemical reactions *in situ*."

Zhou and his colleagues studied the effect of water vapor on the surface of aluminum metal in an effort to better understand mechanistically how the oxide passivation layer forms.

Bilayer oxide film

The researchers worked with thin aluminum foils exhibiting a nominal thickness of approximately 50 nanometers. These materials are prepared using the focused ion beam lift-out technique and the NanoMill system. The foils were atomically cleaned through the use of a condensed electron beam inside the TEM to sputter off native oxide and generate well-defined facets. Deionized water is used in the study and is added to an aluminum foil through a leak valve at a given temperature and gas pressure.

Treatment of clean aluminum foils with various surface orientations and structures, such as [100], [111] and highly stepped surfaces with 3.5 x 10-5 torr of water vapor or liquid water, leads to the formation of oxide on the metal surface. Zhou says, "An initial ETEM observation identifies some kind of surface damage on the aluminum surface. Heat is generated as water is reacting with aluminum metal producing an exotherm. The result is the formation of a surface oxide build-up consisting of aluminum hydroxide as metal atoms are extracted from the topmost layer of the surface. This is the beginning of the formation of a passivation layer which initially is crystalline in nature."

As water vapor continues to encounter the aluminum metal surface, a further transformation of the passivation layer occurs. Zhou says, "Additional water molecules attack deeper into the aluminum substrate eventually resulting in the formation of an amorphous aluminum oxide layer that displaces crystalline aluminum hydroxide. ETEM imaging shows that a crystalline aluminum hydroxide layer remains on top of the amorphous aluminum oxide layer which is adjacent to the metal surface."

A TEM image showing the bilayer oxide film that acts as a passivation layer on aluminum is seen in Figure 1.

Chemical confirmation of the composition of the bilayers was carried out using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). One other issue AP-XPS was able to determine is what happens to the hydrogen atoms that are split from water during the reaction with aluminum. Zhou says, "Using AP-XPS and mass spectroscopy, we found that hydrogen gas is produced during the reaction with aluminum."

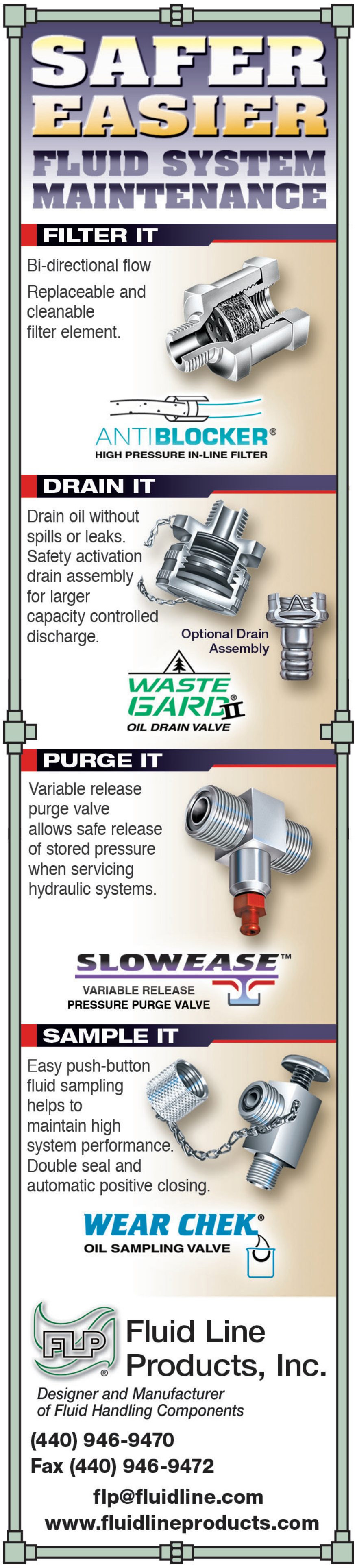
Treatment of water vapor on an aluminum substrate that already has an amorphous aluminum oxide passivation layer produces a crystalline aluminum hydroxide layer. Zhou says, "This experiment proves that the bilayer oxide film is the most thermodynamically, stable passivation layer. Typically, crystalline phases are more stable than amorphous phases. However, the transition of the inner oxide layer to an amorphous phase is thermodynamically favored for several reasons, First, aluminum oxide is more stable than aluminum hydroxide. Additionally, this transition leads to energetically more favorable interfaces both with the aluminum substrate and with the top aluminum hydroxide layer."

The outcome of this work will hopefully lead to the designing of materials that are more stable when exposed to the potential negative effects of water vapor. Zhou says, "We are going to evaluate how other metal alloys interact with water vapor on an atomic scale. Substrates to be evaluated include chrome steel and a nickel/aluminum alloy."

One other phenomenon Zhou will consider evaluating is how the aluminum oxide passivation layer dissipates at pH values above 9. Information produced from this study may help in finding potential additives that can be used to minimize aluminum staining.

Additional information can be found in a recent article[2] or by contacting Zhou at ***gzhou@binghamton.edu***.

1. Canter, N. (2015), "Aluminum alloy acts to inhibit corrosion," TLT, **71** (3), pp. 18-19. Available at **www.stle.org/files/TLTArchives/2015/03_March/Tech_Beat_III.aspx**.
2. Chen, X., Shan, W., Wu, D., Patel, S., Cai, N., Li, C., Ye, S., Liu, Z., Hwang, S., Zakharov, D., Boscoboinik, J., Wang, G. and Zhou, G. (2023), "Atomistic mechanisms of water vapor-induced surface passivation," *Science Advances*, **9** (44), DOI: 10.1126/sciadv.adh5565.



Feasibility of fuel cell powered trucks to support electric grid

A study was conducted to determine if fuel cell powered trucks parked at vehicle-to-grid hydrogen fuel stations can contribute power to the grid in a cost effective manner.

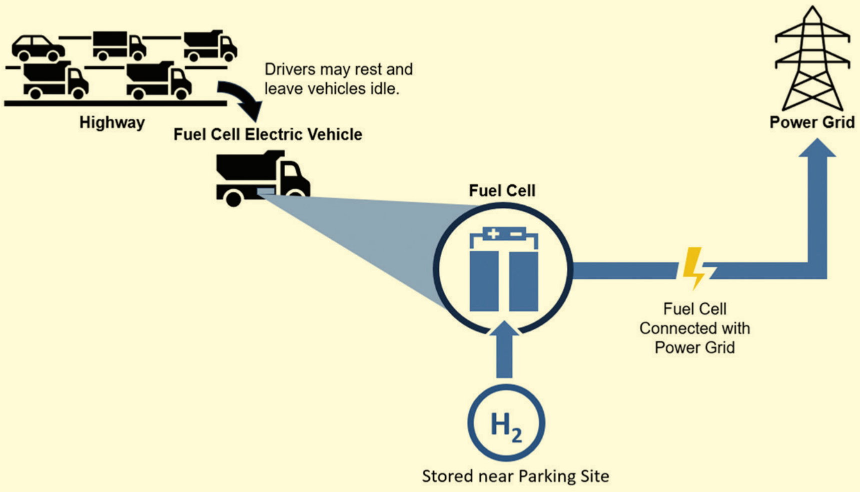


Figure 2. **A schematic shows how fuel cell powered electric vehicles can generate electricity to support a power grid.** *Figure courtesy of Daniel Ding, University of Waterloo.*

HIGHLIGHTS

Heavy-duty trucks powered by fuel cells can be used as portable energy generators to support the electric grid.

A theoretical study found that truck-to-grid hydrogen fuel stations are able to support the electric grid in the Canadian province of Alberta if sufficient trucks are available.

At least four fuel cell powered trucks are needed for the vehicle-to-grid fueling station to be profitable and to generate electricity cleaner than grid electricity.

The transition to electrification is increasing the demand for power, which is stressing electric grids that are not designed to handle this scenario. This trend has led to the growing use of energy storage as a means to support electric grids during times of high demand.

A previous TLT article[1] discusses the implementation of an energy storage technique known as pumped storage hydropower. Water is pumped from a lower reservoir to an upper reservoir during periods when electricity supply is greater than demand. For periods of high demand, the water in the upper reservoir is released to the lower reservoir under the influence of gravity. The potential energy of the water is converted into kinetic energy by driving turbines to generate electricity. The cost of this approach can be reduced through the prefabrication of structural steel modules used in their construction and in using a closed-loop pump storage system to conserve water.

Xiao-Yu Wu, professor in the department of mechanical and mechatronics engineering at the University of Waterloo in Waterloo, Ontario, Canada, says, “Pumped storage hydroelectricity, batteries and hydrogen are examples of energy storage technologies that are feasible but require a large investment in site preparation and device purchases. Figuring out a strategy for storing renewable energy that can be utilized for a long period of time such as the winter season is challenging.”

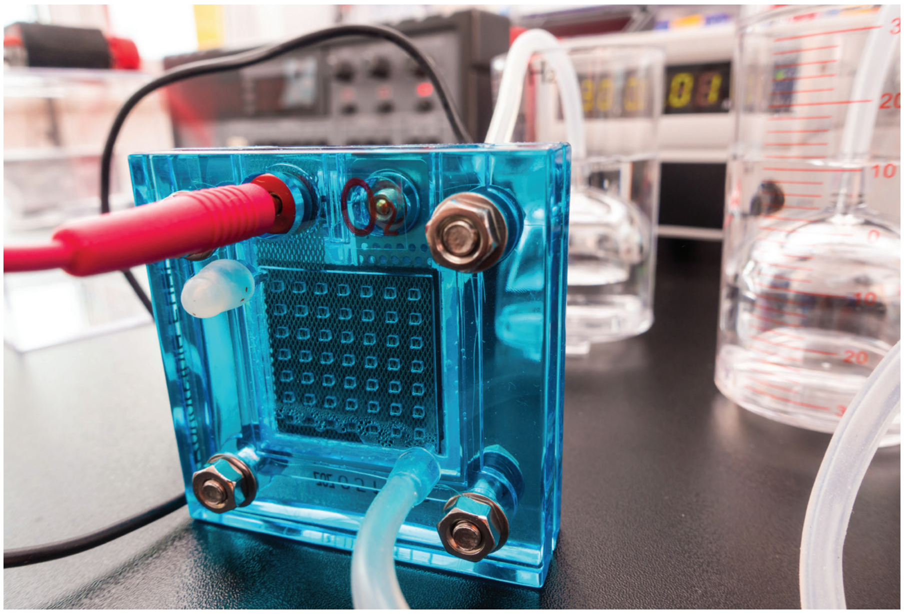
Wu proposes a different strategy to provide power to the electric grid during times of high demand *(see Figure 2)*. He says, “Portable electricity generators are an appealing option if they can generate sufficiently high levels of power to make a difference. The most viable way to achieve this goal is to use heavy-duty trucks that are powered by fuel cells. During periods of inactivity, trucks will be able to park at vehicle-to-grid fueling stations that contain hydrogen produced from renewable energy sources. In effect, hydrogen storage in the station is similar to a gasoline reservoir. The fuel cells in the trucks will then tap into the hydrogen present to generate electricity that can then be sent to the grid.”

Batteries are a less viable option because of their low energy density and longer charging times. In contrast, hydrogen will have a shorter refueling time for trucks, a higher mass-specific energy and power.

Transportation is currently a large source of greenhouse gas emissions. Utilizing fuel cell powered trucks to provide renewable energy to the grid may not only reduce emissions from transportation but also from power generation. Wu says, “In Canada, there is heavy truck traffic on the main highways in the province of Alberta. This area of Western Canada also is highly reliant on fossil fuels for producing electricity. The cost of energy in Alberta also is higher than in other Canadian provinces. These factors led us to conduct a theoretical study to determine if fuel cell powered trucks parked at vehicle-to-grid hydrogen fuel stations can contribute power to the grid in a cost effective manner.

Mixed integer linear programming

Wu and his colleague Daniel Ding, graduate student at the University of Waterloo, produced a theoretical model using mixed integer linear programming that exhibits potential for using vehicle-to-grid hydrogen fuel stations to support the Alberta electric grid if a sufficient number of trucks are acting as electricity generators. In developing the model, the researchers assumed that hydrogen can be sourced either locally from the fuel station (known as grid hydrogen) or from hydrogen pipelines (market hydrogen). The hydrogen manufactured and stored at the fuel station is produced using an onsite electrolyzer powered by excess electricity at night. Market hydrogen originates from a centralized production site that utilizes renewable energy.



Utilizing fuel cell powered trucks to provide renewable energy to the grid may not only reduce emissions from transportation but also from power generation.

Wu says, “Our objective was to maximize the operating profit realized in using fuel cell powered trucks to support the grid. This figure is equivalent to the product of the electricity price and the fuel cell power output minus the cost of the hydrogen feedstock and the cost of the actual fueling process.”

The vehicle-to-grid model operates under several constraints. Wu says, “We are assuming that enough trucks are running to allow for some to be able to act as electricity generators. The power output from the fuel cells of the trucks cannot go above their maximum, and hydrogen stored on site at the vehicle-to-grid fueling station cannot fall below zero or be above its maximum capacity. The hydrogen used cannot come from the truck’s storage tank but from the storage tank on site at the vehicle-to-grid fueling station.”

One benefit is that the use of more trucks leads to a higher demand for market hydrogen reducing carbon dioxide emissions.

Modeling was done by having two, four, six, eight, 10 and 12 trucks contributing electricity to the grid. As part of the analysis, the fuel cells only operated during rush hours, which are assumed to be 7 a.m. to 11 a.m. and 4 p.m. to 8 p.m. local time in Alberta.

The researchers determined that at least four fuel cell powered trucks are needed for the vehicle-to-grid fueling station to be profitable and to generate electricity that is cleaner than grid electricity. They found that operating profit will increase four times when increasing the number of trucks contributing electricity to the grid from two vehicles to 12 vehicles. Fixed costs only increase 2.5 times because increasing the number of fuel cells used to contribute power does not contribute any additional cost.

Another benefit is that the use of more trucks leads to a higher demand for market hydrogen reducing carbon dioxide emissions.

Wu says, “Future work will involve identifying incentives for truckers to use their vehicles to contribute electricity to the grid. We also want to understand how different types of heavy-duty vehicles can contribute electricity to the grid in urban areas. An example is, can snowplows be used to produce electricity during periods when no precipitation occurs?”

Additional information can be found in a recent article[2] or by contacting Wu at ***xiaoyu.wu@waterloo.ca***.

1. Canter, N. (2024), “Energy storage using pumped storage hydropower,” TLT, **80** (2), pp. 12-13. Available at **www.stle.org/files/TLTArchives/2024/02_February/Tech_Beat_I.aspx**.
2. Ding, D. and Yu, X. (2023), “Utilization of fuel cell electric vehicle-to-grid in Alberta by mixed integer linear programming,” 2023 *IEEE the 11th International Conference on Smart Energy Grid Engineering,* DOI:10.119/SEGE59172.2023.10274585.

Multifunctional ionic liquid: A co-catalyst for electrochemical carbon dioxide reduction reaction

Interaction of carbon dioxide gas with an ionic liquid above a copper electrode led to the formation of hydrocarbons.

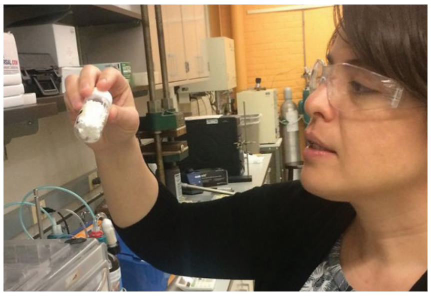


Figure 3. **Professor Burcu Gurkan led a team that utilized a multifunctional ionic liquid as a co-catalyst with copper in facilitating the electrochemical reduction of carbon dioxide.** *Figure courtesy of Case Western Reserve University.*

HIGHLIGHTS

The challenge in reducing carbon dioxide is to convert the molecule from a stable linear to a bent orientation.

A multifunctional ionic liquid known as [EMIM] [2-CNpyr] facilitated carbon dioxide reduction when used with a copper catalyst.

Increasing the concentration of the ionic liquid five-fold led to a two-fold increase in carbon dioxide reduction but a further increase caused the reaction to slow down due to steric constraints.

The desire to reduce the level of the greenhouse gas carbon dioxide in the atmosphere is leading researchers to design pathways for converting this material into useful derivatives that will not contribute to global warming and help close the carbon cycle. One approach that has been under considerable study is the carbon dioxide reduction reaction, which generates useful substances such as hydrocarbons and alcohols.

In a previous TLT article,[1] a photoelectrocatalytic reduction process was developed that not only converts carbon dioxide to syngas (a combination of carbon monoxide and hydrogen), but also oxidizes waste plastic-derived ethylene glycol to glycolic acid. The process was conducted in an aqueous environment using a cobalt (II) phthalocyanine molecular catalyst. Carbon dioxide was captured by an aqueous solution of triethanolamine and then converted to syngas at a cathode that was attached to a perovskite solar cell. To minimize water oxidation, the researchers oxidized ethylene glycol, obtained from polyethylene terephthalate waste, in a separate compartment.

The challenge in reducing carbon dioxide is the stability of the molecule. Oguz Kagan Coskun, a graduate student at Case Western Reserve University in Cleveland, Ohio, says, “Carbon dioxide is a linear molecule which has a very stable structure. Finding a way to make it electrochemically active and allow the initial electron transfer to carbon dioxide is the most energy-demanding step. This high energy requirement is due to the need for the molecule to bend.”

While using an aqueous medium to reduce carbon dioxide is desirable from a sustainability standpoint, water-based systems have limited carbon dioxide capture capacity. In addition, the required potentials for the carbon dioxide reduction reaction trigger a parasitic reaction in the aqueous medium where water is converted to hydrogen gas.

An alternative approach utilized ionic liquids as the electrolyte for facilitating the carbon dioxide reduction reaction. Dr. Saudagar Dongare, postdoctoral researcher at Case Western Reserve University, says, “Functional ionic liquids are a captive medium which can chemically bind with carbon dioxide. They also have been found to modify the surface of catalytic electrodes to form unique double-layer structures. These properties enable ionic liquids to create a microenvironment with reduced potential requirements for carbon dioxide reduction and without the hydrogen evolution reaction.”

Coskun indicates that reaction of the ionic liquid cation and carbon dioxide is more complex. To gain a further understanding of how ionic liquid can promote the reduction of carbon dioxide, Coskun, Dongare and Burcu Gurkan, professor of chemical engineering at the Case Western Reserve School of Engineering *(see Figure 3),* led a study with a specific ionic liquid 1-ethyl-2-methylimidazolium 2-cyanopyrrolide, [EMIM] [2-CNpyr] that they synthesized in the laboratory.

The carbon dioxide reduction reaction was conducted by having the gas and an ionic liquid interact above the surface of a metal electrode which acted as the catalyst. The ionic liquid selected to be used in the electrochemical carbon dioxide reduction reaction, [EMIM] [2-CNpyr], had been found to be active in facilitating the reduction of carbon dioxide in past work.

The researchers found that the catalytic activity is governed by the concentration of the ionic liquid and a natively formed hydrogen bond donor upon chemisorption of carbon dioxide by the ionic liquid.

Copper was used as the catalyst because it has been found to produce hydrocarbon products with high numbers of carbon atoms while reducing carbon dioxide.

Using a variety of analytical techniques, including *in situ* surface-enhanced Raman spectroscopy, electrochemical impedance spectroscopy and linear sweep voltammetry, the researchers found that the catalytic activity is governed by the concentration of the ionic liquid and a natively formed hydrogen bond donor upon chemisorption of carbon dioxide by the ionic liquid. The latter is the anionic component of the ionic liquid. This chemisorption increases the viscosity of the ionic liquid causing mass transport limitations during the reduction reaction.

The viscosity of the ionic liquid plays a role in affecting the reaction rate. To minimize this concern, acetonitrile was introduced as a solvent in the carbon dioxide reduction reaction.

The researchers evaluated the ionic liquid at concentrations ranging from 0.1 to 0.5 molar in acetonitrile. More than a two-fold increase in the reduction of carbon dioxide was realized compared to aqueous systems. When the concentration of the ionic liquid was further increased to 1.0 molar, the reaction slowed down. Gurkan says, "The reason for the reduction in reactivity is steric. As more ionic liquid is present at the copper electrode surface, a thickened double layer structure forms due to its bulky ions. This prevents carbon dioxide from reaching the metal surface effectively."

Products identified from the carbon dioxide reduction reaction included formate, succinate, methane, ethylene and ethane. Gurkan says, "The purpose of the study was to understand the fundamentals of how the ionic liquid affected the rate of the reaction. Future work will be done to increase and understand the factors governing the selectivity."

Additional information can be found in a recent article,[2] by visiting the Gurkan research group website **(www.energylab-cwru.com)**, or by contacting Gurkan at ***beg23@case.edu.***

*Neil Canter heads his own consulting company, Chemical Solutions, in Willow Grove, Pa. Ideas for Tech Beat can be submitted to him at **neilcanter@comcast.net.***

1. Canter, N. (2023), "Production of synthesis gas from carbon dioxide using solar energy," TLT, **79** (10), pp. 22-23. Available at **www.stle.org/files/TLTArchives/2023/10_October/Tech_Beat_III.aspx**.
2. Coskun, O., Dongare, S., Doherty, B., Klemm, A., Tuckerman, M. and Gurkan, B., (2024), Tailoring electrochemical CO_2 reduction on copper by reactive ionic liquid and native hydrogen bond donors," *Angewandte Chemie International Edition* **63** (1), e202312163.