

COBALT NEWS

PUBLISHED BY THE COBALT DEVELOPMENT INSTITUTE

15/4

October 2015

- 2 Comment**
- 3 2015 First Half Production Statistics**
- 5 Kalia Mine Project Update**
- 6 Cobalt could cut Costs for Pharma Ingredients**
- 7 NIST, UC Davis Scientists Float New Approach to Creating Computer Memory**
- 8 Discovery of a Highly Efficient Catalyst Eases Way to Hydrogen Economy**
- 9 New Way to Store Solar Energy Could Lead to More Common Solar Cell Usage**
- 10 Laser-Burned Graphene Gains Metallic Power**
- 11 Spinning Order from Chaos in Metal Alloys**
- 12 A Superhighway for Ions**
- 13 Easily and Effectively Fastening Proteins to Nanoparticles**

COBALT NEWS

CHAIRMAN

D. Elliott (Freeport-McMoRan Sales Co. USA)

VICE CHAIR

T. Litzinger (ICCI, Bahamas)

DIRECTORS

I. Akalay (CTT, Morocco)
H. Gibbs (OMG Americas, USA)
J. Green (Sandvik, USA)
G. Jones (Shepherd Chemicals, UK)
J. Lowe (Dynatec, Madagascar)
M. Oehlers (Shu Powders, China)
V. Mittenzwei (Kennametal, Inc., USA)
M. Majka (Eramet Group, France)
B. Sap (Umicore, Belgium)
F. Schulders (Glencore Intl, Switzerland)
H. Sueta (Sumitomo MM, Japan)
E. Taarland (Chambishi Metals, Zambia)
N. Williams (Vale, Canada)

THE COBALT DEVELOPMENT INSTITUTE

18 Jeffries Passage, Guildford, GU1 4AP, UK

Tel: (0)1483 578877 Fax: (0)1483 567042

email: info@thecdi.com web: www.thecdi.com

Editor: D. Weight – Production: I. Porri

The Cobalt Development Institute carries out activities from a head office in Guildford, UK, to promote the use of cobalt. It is legally incorporated as an association of a wholly non-profit making character in accordance with its memorandum and articles, which are available on request. Membership of the CDI is open to those engaged or interested in the industry, subject to and acceptance by the Board.

Cobalt News exists to disseminate promotion material on uses for, and development in, cobalt technology supported by items of interest to cobalt producers, users and all their customers. Unless otherwise stated as copyright reserved, Cobalt News permits the reprint of articles if fully credited to Cobalt News and its contributors where appropriate.

Comment is the responsibility of the Editor. Views expressed by the contributors are their own. Neither necessarily reflects those of the Institute, its directors or its members.

COMMENT

Since our last Cobalt News 'Comment', the commodity markets have been in a decided slump and mining stock have taken a pounding as investors lose confidence in the power of China to drive demand for raw materials. So all eyes remain firmly fixed on China, however, for future direction.

From our part we are still working hard to try and defend market access for cobalt and we see numerous important issues that could adversely affect cobalt, notably matters related to the REACH Regulation in the EU, particularly the ongoing Authorisation and Restriction activities for salts together with consideration of cobalt on the USA Register of Carcinogens (ROC) following the NTP report on inhalation of cobalt powder, among other things. Central to this is the CDI's scientific position on a threshold mode of action with regard to carcinogenicity, supported strongly by a lack of mutagenicity (refer to OECD Co-CAM Mutual Acceptance of Data in this respect and the Kirkwood review). It is sincerely hoped that Regulators and policy makers pay attention to the scientific work that our industry has done on this subject to ensure a balance and proportionate approach to risk management is adopted – surely the backbone of Regulatory efficiency.

The CDI is a valuable asset for the cobalt industry, identifying issues of importance and addressing these issues on a collective basis, thus saving Member's money and effort. Our value proposition is based on:

- Monitoring Emerging Issues
- Identifying key concerns affecting industry
- Addressing the important issues
- Focusing on results
- Aiming to be the focal point for cobalt

Material is presented for the general information of the reader, and whilst believed to be correct, the CDI, its members, staff and contributors do not represent or warrant its suitability for any general or specific use and assume no liability of any kind in connection with the provision of the said information.

2015 First Half Production Statistics

Table 1 – CDI First Half 2015 Refined Cobalt Production Statistics (Tonnes)

Member companies	2009	2010	2011	2012	2013	2014	2015
Ambatovy, Madagascar	0	0	0	0	1165	1405	1520
BHPB/QNPL, Australia ⁽¹⁾	600	1043	1179	1283	1065	0	0
CTT, Morocco	825	729	910	688	780	606	882
Eramet France	198	181	191	167	172	146	88
Gecamines, DRC ⁽²⁾	199	265	360	380	350	250	200
Glencore ⁽³⁾ :							
Katanga, DRC	0	0	0	0	0	1000	1800
Minara, Australia	0	0	0	0	0	1400	1600
Mopani, Zambia	0	0	0	0	0	0	0
Nikkelverk, Norway ⁽⁴⁾	1609	1580	1404	1388	1600	1700	1500
ICCI, Canada	1876	1744	1838	1947	1558	1463	1709
Freeport Cobalt, Finland (was OMG)	4177	4157	4880	5345	4690	5284	4322
Rubamin, India (Left CDI 2013) ⁽⁵⁾	0	281	295	175	25	0	0
Sumitomo, Japan	507	1041	926	1246	1291	1753	1994
Umicore, Belgium ⁽⁶⁾	1100	1325	1565	2131	2300	2958	3018
Vale, Canada	968	290	1020	1025	1144	937	1090
Zambia ⁽⁷⁾	34	1640	2325	2743	2583	2227	1326
Total	12093	14276	16893	18518	18723	21129	21049

Notes: 1. 2009: BHPB 700mt Jan - Jul and Queensland Nickel Pty (QNPL) 1000mt Aug-Dec. See also Note 12

2. Estimated production; 3. Glencore joined CDI 2014 4. Previously reported as Xstrata, Norway

5. Rubamin joined CDI in 2009 and left in 2013; 6. Includes Umicore's global refined production

7. Chambishi Metals plc Zambia

Production

In Table 1 we show the refined cobalt production from CDI members for the first six months of each calendar year from 2009 to 2015. Glencore joined as Full Members of the CDI in 2014 and so their

tonnage now reports in Table 1. As a result, direct comparisons of total CDI Member production with the previous year are affected accordingly. As shown in the table, total production from CDI member companies for the first half of 2015 was 21,049 tonnes which is slightly down compared to the pre-

Table 2 – CDI First Half 2015 Refined Cobalt Production Statistics (Tonnes)

Non-Member companies	2009	2010	2011	2012	2013	2014	2015
China ⁽⁸⁾	8129	17181	17939	15296	17249	20460	26030
India ⁽⁹⁾	427	310	360	360	125	100	100
Kasese, Uganda	339	314	327	269	291	0	0
Katanga, DRC (See Glencore) ⁽¹⁰⁾	1083	1776	1298	1071	1000	0	0
Minara, Australia (See Glencore) ⁽¹⁰⁾	1084	1008	945	1110	1400	0	0
Mopani, Zambia (See Glencore) ⁽¹⁰⁾	693	600	600	180	0	0	0
Norilsk, Russia ⁽¹¹⁾	1157	1241	1205	1147	1224	1173	1053
QNPL, Australia ⁽¹²⁾				0	0	1177	1047
South Africa ⁽¹³⁾	120	436	440	494	625	705	610
Votorantim, Brazil	399	655	732	846	796	700	700
DLA Deliveries	93	-8	0	0	0	0	0
Total	13524	23513	23846	20773	22710	24315	29540

Notes: 8. Excludes Umicore's refined production in China; 9. Excludes Rubamin between 2009 and 2013

10. From 2014 this reports as Glencore in Table 1; 11. Norilsk ceased to be a CDI member in 2009

12. QNPL ceased to be a CDI Member from 2014; 13. Estimates for RSA Jun production 2015

Table 3 – CDI First Half 2015 Total Refined Cobalt Availability (Tonnes)

	2009	2010	2011	2012	2013	2014	2015
CDI Members	12093	14276	16893	18518	18723	21129	21049
Others	13524	23513	23846	20773	22710	24315	29540
Total⁽¹⁴⁾	25617	37789	40739	39291	41433	45444	50589

Notes: 14. Total Supply does not include any estimates for producers not reporting their production

vious year. Please note that Umicore includes production from their Ganzhou Yi Hao subsidiary in China and this tonnage is therefore not included in the figure for China.

Table 2 summarises refined cobalt production from non-CDI producers together with any deliveries from the DLA stockpile.

As mentioned, refined production attributed to Glencore has now moved into Table 1, so direct comparisons for non-member companies are affected accordingly.

Overall, production from non-CDI producer companies was 29,540 tonnes which represents an increase of 21% when compared to the same period in the previous year. This was largely a result of a 27% increase in refined production recorded by China when compared to the first half of 2014. We have no further information on any connotative stockpiles of cobalt that might exist in China (see the annual CDI statistics which appeared in the April 2012 edition of the Cobalt News). However, we are aware from general press coverage that metal stockpiles in China are being drawn down. As previously mentioned the Chinese refined production shown in Table 2 does not include Umicore's production in China, which is included in Table 1.

The DLA reports its figures slightly differently from the past and the figure shown is *the 'change in uncommitted inventory'* and should be similar to the old DLA *'delivery'* figure we had reported in previous years. There have been no sales over the period and therefore the DLA inventory at the end of June 2015 remains at 301 tonnes. It is understood that the DLA cobalt Basic Ordering Agreement sales program has been deactivated until further notice (DLA Strategic Metals news release of March 11, 2011).

The total availability of refined cobalt in the first half of the year from 2009 to 2015 is shown in Table 3. The figures show that overall availability in the first half of 2015 was 50,589 tonnes over 11% higher than the same period in 2014, largely as a result of the increase in Chinese refined production. This follows on from a ~10% increase when reporting these figures at this time last year. As in the past, we emphasise that the figures do not include production of refined cobalt from companies treating various cobalt-containing intermediate products and scrap that do not report their figures.

Demand

The CDI has published supply and apparent demand data in the WBMS/CDI "World Cobalt Statistics 2012-2014". The data were derived from worldwide import/export figures. The publication details apparent worldwide refined cobalt demand by geographical location. It can be purchased from either the CDI or WBMS. Please see website 'Publications' for details.

In 2014, apparent worldwide demand totalled around 82,000 tonnes, which is about 10% higher than the previous year. As mentioned, the publication can be purchased from either the CDI or the WBMS. See this website for details.

Price

The HG (LMB) price opened 2015 at US\$14.30/lb (compared with US\$12.45/lb for 2014) and at the end of September was US\$13.03/lb. The LG (LMB) price opened at US\$14.15/lb (compared to US\$12.35/lb in 2014) and at the end of September was US\$12.80/lb. The 2015 average HG price to end September is US\$13.76/lb and for LG it is US\$13.55/lb (the CDI takes the average bid/offer spread for both the HG and LG Metal Bulletin price quotation when calculating its average price). A particularly notable feature over the past two years is the narrowing of the spread between HG and LG as the demand for chemical grade cobalt continued to increase ahead of metal.

Cobalt has traded on the LME since February 2010 with the 3M contract which was joined by cash trading in May of that year. The average LME cash price for 2015 to end September is US\$13.37/lb (the CDI takes the average daily bid/offer cash spread for cobalt and averages this over the period). The C-3 spread varied between a US\$550/tonne contango and a US\$1,000/tonne backwardation with an average spread for period of about US\$47/tonne in contango.

Kalia Mine Project Update

Bellzone Mining plc (AIM:BZM) is pleased to announce a new Mineral Resource Estimate ("MRE") reported in accordance with the JORC Code (2012) by CSA Global Pty Ltd ("CSA Global"). The MRE is focused on areas of the Kalia Project where nickel mineralisation occurs in conjunction with iron within the laterite profile.

Highlights:

- **Total nickel Mineral Resources of 79.28 million tonnes at 0.69% Ni and 0.044% Co at a 0.50% nickel cut-off grade**
- **Indicated Mineral Resource of 27.43 million tonnes at 0.70% Ni and 0.037% Co**
- **Inferred Mineral Resources of 51.85 million tonnes at 0.68% Ni and 0.047% Co**
- **Supports further study to be carried out on developing a modular nickel pig iron ("NPI") production facility on site**

In the evaluation of Ore Reserves in an area known as Kalia Northwest (Kalia NW) for the Company's 100 per cent. owned Kalia Project 1, it was noted that in certain areas, weathering processes have formed an iron (goethite/haematite) and nickel-

enriched laterite profile over an underlying ultramafic intrusion. In addition to high iron content, many samples within the weathering profile have nickel mineralisation consistent with lateritic enrichment, with values up to 2.5% Ni being recorded.

On 15 July 2015 Bellzone published an update announcing that a strategic review had highlighted the presence of nickel laterite mineralisation at Kalia NW. Bellzone recognised that this provided a potential alternative pathway to commence iron ore mining at Kalia, producing nickel pig iron ("NPI") or ferronickel on site. The Company commissioned CSA Global to commence work on an initial MRE under the JORC Code (2012). CSA Global has now completed and provided Bellzone with its MRE report that confirms a maiden nickel JORC Mineral Resource Estimate. Initial scoping by Bellzone suggests that the quantity of resources is more than adequate to support further studies to assess the viability of developing a modular NPI or ferronickel production facility in Guinea. The new MRE is based solely on data collected during the iron exploration phase of the project.

The nickel mineralisation occurs in two related but distinct rock types:

Category	Tonnes Mt	Mineral Resources Contained metal			Grades									
		Iron ore Mt	Ni Kt	Co Kt	Ni %	Co %	Fe %	SiO ₂ %	Al ₂ O ₃ %	MgO %	P %	S %	LOI %	
		Fe-Ni mineralisation												
Indicated	27.43	27	191	10.2	0.70	0.037	54.54	2.83	4.04	0.64	0.09	0.03	10.45	
Inferred	15.64	16	102	6.0	0.65	0.039	54.39	3.59	3.71	0.79	0.06	0.02	9.99	
Sub-Total	43.07	43	293	16.2	0.68	0.038	54.48	3.11	3.92	0.70	0.08	0.03	10.28	
Ni mineralisation														
Inferred	36.21		251	18.4	0.69	0.051	37.02	21.56	3.08	7.58				
Sub-Total	36.21		251	18.4	0.69	0.051	37.02	21.56	3.08	7.58				
TOTAL	79.28		544	34.6	0.69	0.044	46.51	11.54	3.54	3.84				

Notes:

1. Mineral Resources were estimated within constraining wireframes based on Ni > 0.5% cut-off grade and Fe > 48% cut off grade per resource block for iron ore resources.
2. Mineral Resources are classified according to the JORC Code.
3. Dry bulk density is 1.6 t/m³ for laterite and transition zones and 1.8 t/m³ for saprolite and saprock zones
4. Rows and columns may not add up exactly due to rounding
5. The above Nickel-Iron Resource tonnages should be excised from the main Iron resource tonnages in the Published Iron Ore Resources.

- transition and massive laterite zones in which some of the iron ore resources published by Bellzone in August 2013 (“Published Iron Ore Resources”) occur (“Nickel-Iron ore Mineral Resources”); and

- saprolites and saprock adjacent to the Published Iron Ore Resources (“Nickel Mineral Resources”)

Both types of mineralisation have been estimated and are shown in the above table.

KH Tung, Chief Executive Officer of Bellzone said “The nickel JORC Mineral Resource Estimate confirms the potential for Bellzone to commence the development of the Kalia iron ore mine with downstream processing of iron ore in Guinea to produce a higher value iron ore product with a high nickel content. We will also assess the potential contribution that the cobalt content in the mineralisation provides.”

“We have identified a pathway to development of KP1 and on to the development of the greater Kalia project. The Board will consult with stakeholders and determine the next steps to progress the study and we look forward to providing further updates as the strategic review progresses.”

Competent Person Statements:

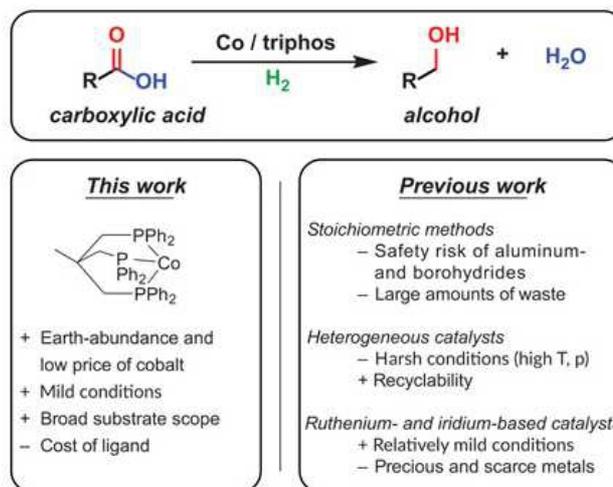
The information in this announcement that relates to the Nickel Mineral Resource at Kalia is based on information compiled by Mr Mick Elias of CSA Global. Mr Elias takes overall responsibility for the Mineral Resource estimates. Mr Elias is a member of the Australian Institute of Geoscientists and has 35 years of experience which is relevant to the style of mineralisation and type of deposit under consideration, and to the activity he is undertaking, to qualify as a Competent Person in terms of the “Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves (JORC Code 2012 Edition)”. Mr Elias has reviewed the information contained in this announcement and consents to the inclusion of such information in this announcement in the form and context in which it appears.

Enquiries: Bellzone Mining plc +44 (0) 1534 513 500
Simon Edwards

WH Ireland Limited
Nominated Adviser
James Joyce / James Bavister
+44 (0) 20 7220 1666

HD Capital Partners Limited
Broker
Paul Dudley / Philip Haydn Slater
+44 (0) 20 3551 4870

Cobalt could cut costs for pharma ingredients



© Science/AAAS

Researchers in the Netherlands have developed a cobalt catalyst that can be used in the hydrogenation of esters and carboxylic acids to alcohols without the need for extremely high temperatures or expensive precious metals.

Bas de Bruin and colleagues at the University of Amsterdam tried out different catalysts made by combining commercially available cobalt salts with a tridentate phosphine ligand in the hydrogenation of methyl benzoate to benzyl alcohol and methanol. The best performing system, which produced high yields under relatively mild conditions, used cobalt tetrafluoroborate hexahydrate ($Co(BF_4)_2 \cdot 6H_2O$) as the cobalt precursor. Currently, carboxylic acid hydrogenations – which are used in the synthesis of a variety of desirable compounds including materials and pharmaceuticals – have to be carried out using heterogeneous catalysts at high temperatures and pressures, or far more costly precious metal catalysts based on iridium or ruthenium.

The group say the development, which follows other recent advances in the development of iron and cobalt catalysts for hydrogenation of alkenes, imines and ketones, may enable the production of more high-value chemicals from biomass, as well as making various industrial syntheses more cost-effective.

References

T J Korstanje *et al*, *Science*, 2015, DOI: 10.1126/science.aaa8938

This story by Emma Stoye was first posted on Chemical World on 15 October 2015 <http://www.rsc.org/chemistryworld/2015/10/cobalt-catalyst-enables-low-cost-hydrogenation-carboxylic-acids-esters>

NIST, UC Davis Scientists Float New Approach to Creating Computer Memory

What can skyrmions do for you? These ghostly quantum rings, heretofore glimpsed only under extreme laboratory conditions, just might be the basis for a new type of computer memory that never loses its grip on the data it stores.

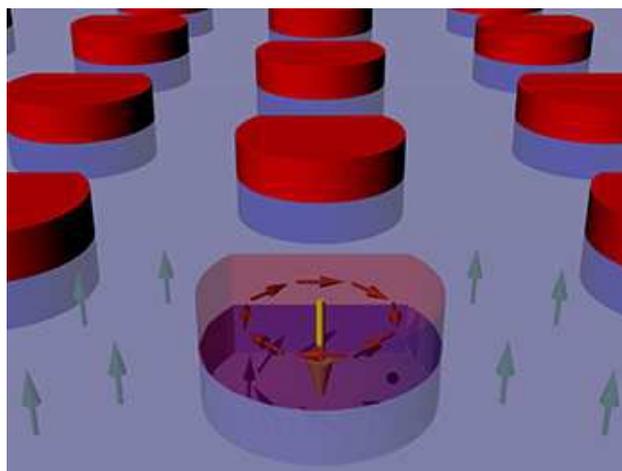
Now, thanks to a research team including scientists from the National Institute of Standards and Technology (NIST),* the exotic ring-shaped magnetic effects have been coaxed out of the physicist's deepfreeze with a straightforward method that creates magnetic skyrmions under ambient room conditions. The achievement brings skyrmions a step closer for use in real-world data storage as well as other novel magnetic and electronic technologies.

If you have a passing familiarity with particle physics, you might expect skyrmions to be particles; after all, they sound a lot like fermions, a class of particles that includes protons and neutrons. But skyrmions are not fundamental pieces of matter (not even of yogurt); they are effects named after the physicist who proposed them. Until just recently, magnetic skyrmions had only been seen at very low temperatures and under powerful magnetic fields.

The magnetic force in each individual atom in a magnet—what physicists call their “magnetic moments”—all line up the same way, like tiny compasses all pointing in the same direction. But under extreme conditions, certain magnetic materials (such as MnSi or FeCoSi) can, instead, develop spots where the moments curve and twist, forming a winding, ring-like configuration. These unusual objects possess an elasticity that protects them from outside influence, meaning the data they store would not be corrupted easily, even by stray magnetic fields or physical defects within the material. As a result, magnetic skyrmions present a promising basis for information memory systems and other nanoelectronic devices.

A hurdle in using traditional skyrmions was the extreme lab conditions needed to form them. Until recently, scientists glimpsed magnetic skyrmions only at low temperatures. While NIST's Dustin Gilbert was a graduate student in Kai Liu's lab at the University of California, Davis, he and Liu not only designed an approach to make the quantum objects, but also their creations remained stable at room temperature, with no magnetic field.

It took a trip to NIST to confirm the skyrmions' existence. Creating them involves placing arrays of tiny magnetized cobalt disks atop a thin film made of cobalt and palladium; the NIST Center for Neutron



A magnetized cobalt disk (red) placed atop a thin cobalt-palladium film (light purple background) can be made to confer its own ringed configuration of magnetic moments (orange arrows) to the film below (purple arrows), creating a skyrmion in the film. The skyrmion, which is stable at room temperature, might be usable in computer memory systems. Credit: Dustin Gilbert/NIST

Research (NCNR) had just developed a state-of-art polarized neutron reflectometer that was well suited to study their lab results. Working with NCNR scientists, the team used neutrons to see through the disk to spot the skyrmions underneath. The team also captured images of the whirling configurations in the disk array at NIST's Center for Nanoscale Science and Technology (CNST) and Lawrence Berkeley Laboratory.

According to Gilbert, the findings should interest anyone following spintronics, a field that aims to use magnetic effects such as those skyrmions exhibit for information storage and processing.

“The idea that has been discussed is that, for example, you could just push these stable magnetic bundles in single file down a line and read their data. The advantage here is that you'd need way less power to push them around than any other method proposed for spintronics,” says Gilbert, who recently began a postdoctoral fellowship at the NCNR. “What we need to do next is figure out how to make them move around. But for now, we can start exploring how we might use skyrmions in technology—the playground is open.”

*D.A. Gilbert, B.B. Maranville, A.L. Balk, B.J. Kirby, P. Fischer, D.T. Pierce, J. Unguris, J.A. Borchers and K. Liu. Realization of Ground State Artificial Skyrmion Lattices at Room Temperature. *Nature Communications*, 6:8462, doi: 10.1038/ncomms9462 (2015).

First posted on www.nist.org on 8 October 2015 (<http://www.nist.gov/ncnr/20151008skyrmions.cfm>)

Discovery of a highly efficient catalyst eases way to hydrogen economy

Hydrogen could be the ideal fuel: Whether used to make electricity in a fuel cell or burned to make heat, the only byproduct is water; there is no climate-altering carbon dioxide.

Like gasoline, hydrogen could also be used to store energy.

Hydrogen is usually produced by separating water with electrical power. And although the water supply is essentially limitless, a major roadblock to a future "hydrogen economy" is the need for platinum or other expensive noble metals in the water-splitting devices.

Noble metals resist oxidation and include many of the precious metals, such as platinum, palladium, iridium and gold.

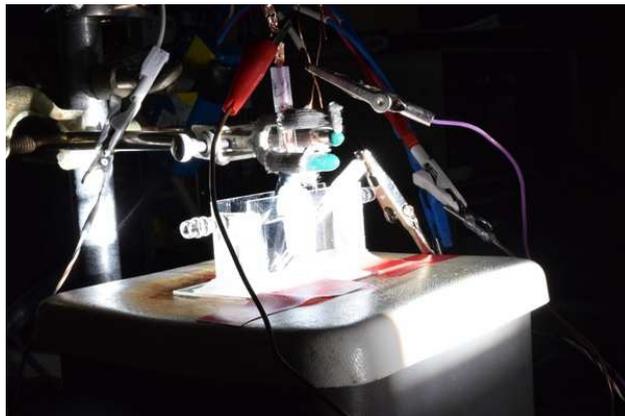
"In the hydrogen evolution reaction, the whole game is coming up with inexpensive alternatives to platinum and the other noble metals," says Song Jin, a professor of chemistry at the University of Wisconsin-Madison.

In the online edition of *Nature Materials* that appears today, Jin's research team reports a hydrogen-making catalyst containing phosphorus and sulfur — both common elements — and cobalt, a metal that is 1,000 times cheaper than platinum. Catalysts reduce the energy needed to start a chemical reaction. The new catalyst is almost as efficient as platinum and likely shows the highest catalytic performance among the non-noble metal catalysts reported so far, Jin reports.

The advance emerges from a long line of research in Jin's lab that has focused on the use of iron pyrite (fool's gold) and other inexpensive, abundant materials for energy transformation. Jin and his students Miguel Cabán-Acevedo and Michael Stone discovered the new high-performance catalyst by replacing iron to make cobalt pyrite, and then added phosphorus.

Although electricity is the usual energy source for splitting water into hydrogen and oxygen, "there is a lot of interest in using sunlight to split water directly," Jin says. "If you want to make a dent in the global warming problem, you have to think big."

The new catalyst can also work with the energy from sunlight, Jin says. "We have demonstrated a proof-of-concept device for using this cobalt catalyst and solar energy to drive hydrogen generation, which also has the best reported efficiency for systems that



Bathed in simulated sunlight, this photoelectrolysis cell in the lab of Song Jin splits water into hydrogen and oxygen using a catalyst made of the abundant elements cobalt, phosphorus and sulphur. Photos: David Tenenbaum

rely only on inexpensive catalysts and materials to convert directly from sunlight to hydrogen."

Many researchers are looking to find a cheaper replacement for platinum, Jin says. "Because this new catalyst is so much better and so close to the performance of platinum, we immediately asked WARF (the Wisconsin Alumni Research Foundation) to file a provisional patent, which they did in just two weeks."

Many questions remain about a catalyst that has only been tested in the lab, Jin says. "One needs to consider the cost of the catalyst compared to the whole system. There's always a tradeoff: If you want to build the best electrolyzer, you still want to use platinum. If you are able to sacrifice a bit of performance and are more concerned about the cost and scalability, you may use this new cobalt catalyst."

Strategies to replace a significant portion of fossil fuels with renewable solar energy must be carried out on a huge scale if they are to affect the climate crisis, Jin says. "If you want to make a dent in the global warming problem, you have to think big. Whether we imagine making hydrogen from electricity, or directly from sunlight, we need square miles of devices to evolve that much hydrogen. And there might not be enough platinum to do that."

The collaborative team included Professor J.R. Schmidt, a theoretical chemist at UW-Madison, and electrical engineering Professor Jr-Hau He and his students from King Abdullah University of Science and Technology in Saudi Arabia. The U.S. Department of Energy provided major funding for the study.

Story written by David Tenenbaum and first posted on <http://news.wisc.edu/24010> on 14/09/2015

New way to store solar energy could lead to more common solar cell usage

Researchers at Missouri University of Science and Technology have developed a relatively inexpensive and simple way to split water into hydrogen and oxygen through a new electrodeposition method. The method produces highly efficient solar cells that can gather solar energy for use as fuel.

The research, sponsored by the U.S. Department of Energy, could lead to a sizable increase in the amount of hydrogen available for fuel usage.

The Missouri S&T researchers describe their full method in a paper published today (Monday, Sept. 14, 2015) on the website of the journal *Nature Materials*.

“The work helps to solve the problem that solar energy is intermittent,” says Dr. Jay A. Switzer, the Donald L. Castleman/Foundation for Chemical Research Professor of Discovery at Missouri S&T. “Obviously, we cannot have the sun produce energy on one spot the entire day, but our process converts the energy into a form that is more easily stored.”

Switzer and his team use silicon wafers to absorb solar energy. The silicon is submerged in water, with the front surface exposed to a solar energy simulator and the back surface covered in electrodes to conduct the energy. The silicon has cobalt nano-islands formed onto it using a process called electrodeposition.

Unlike current research standards that cover the surface of the silicon entirely in a catalyst layer, Switzer has small clusters of cobalt catalysts dotted on the silicon’s surface. This process was found to be just as protective and produced much higher voltages.

The generated voltage from the solar rays splits liquid water into hydrogen and oxygen. Oxygen evolves at the cobalt-coated silicon electrode, and hydrogen evolves at the platinum counter electrode. “Initially, we had set out to produce a uniform layer of metal that both catalyzed and protected the silicon, but found that this method actually produces a higher voltage and did not need an additional step that typically has to be applied to the silicon,” says Switzer. “These nano-islands of cobalt produce a much more efficient cell.”

Besides solar arrays and energy cells, Switzer sees potential usage of the results in large-scale

hydrogen collection and even a fully carbon-neutral travel solution.



A working cell from Switzer’s research, with gas evolution. Photo by Sam O’Keefe, Missouri S&T.

“If we use this process in hydrogen-fueled vehicles, the hydrogen would be used as fuel and the only thing dripping out of the tailpipe of the car would be water,” says Switzer.

Switzer’s co-authors of the paper, titled “An electrodeposited inhomogeneous metal–insulator–semiconductor junction for efficient photoelectrochemical water oxidation,” are James C. Hill, a post-doctoral fellow at Missouri S&T, and Alan T. Landers, a 2015 chemistry graduate of Missouri S&T.

Story by Peter Ehrhard first posted on <http://news.mst.edu/2015/09/new-way-to-store-solar-energy-could-lead-to-more-common-solar-cell-usage/> on 15 September 2015.

Laser-burned graphene gains metallic powers

Rice University scientists find possible replacement for platinum as catalyst

HOUSTON – (Aug. 20, 2015) – Rice University chemists who developed a unique form of graphene have found a way to embed metallic nanoparticles that turn the material into a useful catalyst for fuel cells and other applications.

Laser-induced graphene, created by the Rice lab of chemist James Tour last year, is a flexible film with a surface of porous graphene made by exposing a common plastic known as polyimide to a commercial laser-scribing beam. The researchers have now found a way to enhance the product with reactive metals.

The research appears this month in the American Chemical Society journal ACS Nano.

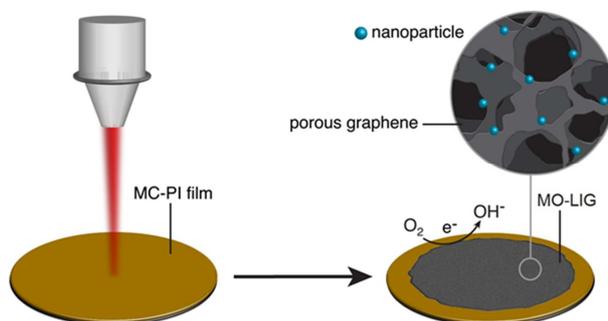
With the discovery, the material that the researchers call “metal oxide-laser induced graphene” (MO-LIG) becomes a new candidate to replace expensive metals like platinum in catalytic fuel-cell applications in which oxygen and hydrogen are converted to water and electricity.

“The wonderful thing about this process is that we can use commercial polymers, with simple inexpensive metal salts added,” Tour said. “We then subject them to the commercial laser scribe, which generates metal nanoparticles embedded in graphene. So much of the chemistry is done by the laser, which generates graphene in the open air at room temperature.

“These composites, which have less than 1 percent metal, respond as ‘super catalysts’ for fuel-cell applications. Other methods to do this take far more steps and require expensive metals and expensive carbon precursors.”

Initially, the researchers made laser-induced graphene with commercially available polyimide sheets. Later, they infused liquid polyimide with boron to produce laser-induced graphene with a greatly increased capacity to store an electrical charge, which made it an effective supercapacitor.

For the latest iteration, they mixed the liquid and one of three concentrations containing cobalt, iron or molybdenum metal salts. After condensing each mixture into a film, they treated it with an infrared laser and then heated it in argon gas for half an hour at 750 degrees Celsius.



Rice University chemists have found a way to embed metallic nanoparticles into laser-induced graphene. The particles turn the material into a useful catalyst for fuel cell and other applications. (Credit: Tour Group/Rice University)

That process produced robust MO-LIGs with metallic, 10-nanometer particles spread evenly through the graphene. Tests showed their ability to catalyze oxygen reduction, an essential chemical reaction in fuel cells. Further doping of the material with sulfur allowed for hydrogen evolution, another catalytic process that converts water into hydrogen, Tour said.

“Remarkably, simple treatment of the graphene-molybdenum oxides with sulfur, which converted the metal oxides to metal sulfides, afforded a hydrogen evolution reaction catalyst, underscoring the broad utility of this approach,” he said.

Rice graduate student Ruquan Ye and Rice alumnus Zhiwei Peng, now a postdoctoral researcher at the University of Maryland, are lead authors of the paper. Co-authors are Rice graduate students Tuo Wang, Jibo Zhang and Lizanne Nilewski; Rice undergraduate Yunong Xu; and Rice alumnus Jian Lin, an assistant professor of mechanical and aerospace engineering at the University of Missouri. Tour is the T.T. and W.F. Chao Chair in Chemistry as well as a professor of materials science and nanoengineering and of computer science and a member of Rice’s Smalley-Curl Institute.

The Air Force Office of Scientific Research and its Multidisciplinary University Research Initiative supported the research.

This story by Mike Williams was posted on <http://news.rice.edu> on 20 August 2015 (<http://news.rice.edu/2015/08/20/laser-burned-graphene-gains-metallic-powers/>)

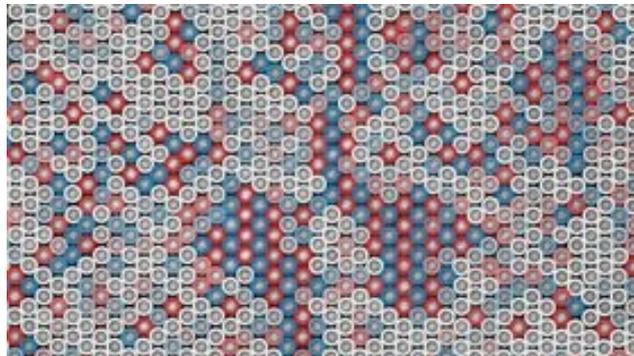
Spinning order from chaos in metal alloys

Electron spin can bring order out of chaos, that's a prediction regarding the ordering of Cr in an equiatomic fcc NiFeCrCo high entropy alloy (HEA) according to research by a team of scientists at North Carolina State University and Furman University, South Carolina, USA. The team tested these predictions through the synthesis of three samples by casting/annealing or milling. The samples exhibited low temperature magnetic moments consistent with trends from the first principles simulations and advanced scanning transmission electron microscopy identified ordered nano-domains. [Niu et al., *Appl Phys Lett*, 2015, **106**, 161906; DOI: 10.1063/1.4918996]

HEAs, with their four or more metals present in approximately equal amounts, have some intriguing magnetic and mechanical properties and have become the focus of much research during the last decade or so, according to NC State materials scientist Doug Irving. "For example, NiFeCrCo-based HEAs have a good combination of hardness, tensile strength, ductility, and fracture resistance at extremely low temperatures," Irving explains. "If you look at NiFeCrCo, it has a fixed structure, but which atoms fill each site is seemingly random - it seems impossible to predict which element might be in any given site." That impression of chaos is why they're called high entropy alloys.

Irving and his team have now demonstrated that there is greater order in this chaos than was previously imagined and it is the spins of the electrons on chromium atoms that drive this order. It is well known that electron spins can be aligned in the same direction in ferromagnetic materials - cobalt, iron and nickel. Conversely in antiferromagnetic materials, such as chromium, spins align in the opposite direction to their neighbours.

To complicate matters, in an HEA such as NiFeCrCo, spins on the chromium electrons can align against their neighbours if they are surrounded by iron, nickel or cobalt. Those three metals can display all spins up while chromium has spin down. However, if two chromium atoms are themselves neighbours they cannot of course align their spins differently from all of their neighbours because they themselves are neighbours. The result is that the spin properties of chromium force the chromium atoms to reside in the HEA with the greatest separation possible. This results in nanoscopic domains of order within the overall chaos of the HEA.



"Showing that this material has order at the nanoscale will likely lead to new work on how to expand these ordered domains, and potentially manipulate the material's mechanical properties," Irving explains.

Irving told *Materials Today* about a few future directions. "The first would be the impact of this local ordering on properties of the alloy," he says. "What role does local order play in the remarkable mechanical properties? Additionally, it would be interesting to analyze how this extends to systems with more components where multiple elements are anti-ferromagnetic."

This story by David Bradley was first posted on www.materialstoday.com (<http://www.materialstoday.com/metals-alloys/news/spinning-order-from-chaos-in-metal-alloys/>) on 8 May 2015. David Bradley blogs at [Sciencebase Science Blog](#) and tweets @sciencebase, he is author of the popular science book "Deceived Wisdom".

A superhighway for ions

You're going to have to think very small to understand something that has the potential to be very big.

A team of researchers, including Kyle Brinkman of Clemson University, developed a material that acts as a superhighway for ions. The material could make batteries more powerful, change how gaseous fuel is turned into liquid fuel and help power plants burn coal and natural gas more efficiently.

Ye Lin, Shumin Fang and Fanglin Chen, all of the University of South Carolina, collaborated with Brinkman and Dong Su, who is with the Center for Functional Nanomaterials at Brookhaven National Laboratory in Upton, New York.

To understand what they did, it helps to know how batteries and fuel cells convert chemical energy into electricity.

It goes like this: A chemical reaction splits fuel atoms into ions and electrons. The ions go through a substance called an electrolyte while electrons zip around a circuit. When the ions and electrons recombine on the other side of the electrolyte, it creates electrical power.

That's why your cell phone is able to light up or your iPod starts playing music.

Batteries and fuel cells have done some great stuff, but they are limited by how fast ions pass through the electrolyte. If you speed up the ions, you'll have a more powerful battery or fuel cell. The challenge for engineers is finding a mix of electrolyte ingredients that allows the ions to move as quickly as possible.

Members of the research team sharpened their focus on ceria doped with gadolinia. It's not something you buy at the local convenience store, but it's a substance well-known to materials scientists and engineers. Seen through a highly powerful microscope, the material looks like a chessboard with many particles, or "grains," jammed together. Those grains are made of gadolinia-doped ceria, and ions zip through the grains with ease.

But there was a problem. Gadolinia tends to accumulate at the boundaries of those tiny grains, slowing down the ions.

The research team figured out that adding cobalt iron oxide to the mix cleaned out the gadolinium that had accumulated in the grain boundaries. With the new ingredient, ions had clear sailing through the electrolyte en route to their rendezvous with the electrons. It's great for turning chemical energy into

electrical power, which could result in more powerful batteries and fuel cells. But that's not all.

Cleaning out the boundaries allowed easier movement of oxygen ions, which helps create pure oxygen. So the same material that enhances power could also be used to create membrane systems that purify gas mixtures. It could mean that oxygen will replace steam in the process used to turn fuels into liquid, including the gasoline you put in your car. Pure oxygen is also an ideal environment for fire, so it could be used to help burn coal and natural gas.

Brinkman said he first began working on the technology when he was a post-doctoral researcher at the National Institute of Advanced Industrial Science and Technology in Japan. He continued his work at Savannah River National Laboratory and brought it with him when he took the job at Clemson in January 2014. Brinkman is now an associate professor in the materials science and engineering department.

"I'm proud to be a part of this collaboration," he said. "It's a great feeling to understand the principles and to know they can be applied. I think we're on the cusp of something potentially world-changing.

"The ability to control the performance of materials by tuning small interfacial regions represents a huge opportunity in the design of materials for use in energy conversion and storage."

When he first began his research, Brinkman would mix various materials together, take measurements and try to understand what happened based on equations.

But now researchers can see what is occurring at the atomic level by using Brookhaven's highly powerful electron microscopes.

This story was posted on www.materialstoday.com (<http://www.materialstoday.com/energy/news/a-superhighway-for-ions/>) on 14 April 2015 and was reprinted from material from Clemson University, with editorial changes made by Materials Today. The views expressed in this article do not necessarily represent those of Elsevier.

Easily and effectively fastening proteins to nanoparticles

Fastening protein-based medical treatments to nanoparticles isn't easy. With arduous chemistry, scientists can do it. But like a doomed marriage, the fragile binding that holds them together often separates.

This problem, which has limited how doctors can use proteins to treat serious disease, may soon change. University at Buffalo researchers have discovered a way to easily and effectively fasten proteins to nanoparticles – essentially an arranged marriage – by simply mixing them together.

While in its infancy, the model already has shown promise for developing an HIV vaccine and as a way to target cancer cells.

"Scientists have been able to attach proteins to nanoparticles for a while now. But it's a fairly difficult process that's only effective in a controlled environment.

Nobody has been able to devise a simple method that can work inside the body," said Jonathan F. Lovell, PhD, UB assistant professor of biomedical engineering, who led the research.

He added: "We have proven that you can easily attach proteins to nanoparticles and, like Velcro that doesn't unstick, it stays together."

To create the biotechnology, the researchers use nanoparticles made of chlorophyll (a natural pigment), phospholipid (a fat similar to vegetable oil) and cobalt (a metal often used to prepare magnetic, water-resistant and high-strength alloys).

The proteins, meanwhile, are modified with a chain of amino acids called a polyhistidine-tag. Uncommon in medicine, polyhistidine-tags are used extensively in protein research.

Next, the researchers mixed the modified proteins and nanoparticles in water. There, one end of the protein embeds into the nanoparticle's outer layer while the rest of it sticks out like a tentacle.

To test the new binding model's usefulness, the researchers added to it an adjuvant, which is an immunological agent used to enhance the efficacy of vaccines and drug treatments. The results were impressive. The three parts – adjuvant, protein and nanoparticle – worked together to stimulate an immune response against HIV.

The researchers also tested proteins that target cancer cells. Again, the results were exciting, with the new binding model acting like a homing missile to tumors. The targeted nanoparticles have the potential to improve cancer treatment by targeting specific cancer cells in lieu of releasing

anti-cancer drugs everywhere in the body.

Lovell plans to follow up the research with more rigorous testing of the vaccine and tumor-targeted technologies. Moving to human clinical trials is the ultimate goal.

This story was posted on www.materialstoday.com on 21 April 2015 (<http://www.materialstoday.com/amorphous/news/fastening-proteins-to-nanoparticles/>) and was reprinted from material from University at Buffalo, with editorial changes made by Materials Today. The views expressed in this article do not necessarily represent those of Elsevier.

"We have proven that you can easily attach proteins to nanoparticles and, like Velcro that doesn't unstick, it stays together."

*Jonathan F. Lovell, PhD, UB
assistant professor of biomedical
engineering.*