

# NERGY FOCU

# **Energy Spotlight**

# Personal Reflections of Energy Researchers on the 2019 Chemistry Nobel Laureates

he electrochemistry, materials science and engineering, and energy research communities were thrilled this year to hear the news of the 2019 Chemistry Nobel Prize being awarded to Profs. John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino. For the past several years, anticipation that they would be awarded the Nobel Prize became an annual routine in early October. With each passing year, upon hearing the news that the Nobel Prize in Chemistry went to another discipline instead of storage batteries, we began to anticipate the same remarks such as, why battery research is not "good enough" for the Nobel prize. When the announcement came this year, social media exploded with exuberance. Entire energy research communities celebrated the recognition given to these pioneers of Li-ion batteries. Because Li-ion batteries have become an integral part of our everyday life, there was no need to explain to a nonchemist what this year's Nobel Prize was about. Everyone immediately understood the significance, the broad ranging societal impact of this advancement in chemistry, and the recognition it deserved.

To celebrate this recognition and congratulate the 2019 Chemistry Nobel Prize winners, ACS Energy Letters asked a few energy researchers, including our EAB members, to share their personal stories and reflections highlighting their interactions with these Nobel Laureates and the inspiration they received from their work.

### "STAN THE MAN"



The research team at North East Center for Chemical Energy Storage (NECCES), Binghamton University (Photo courtesy: Louis Piper)

"Oh, where Stan works!" would often be a typical reply whenever I introduced myself with my affiliation. The followup responses would often ask about his Nobel prize chances. My first reaction when I heard the breaking news was that his Nobel prize was long overdue. His seminal paper in 1976 on energy storage using Li-ion intercalation truly transformed society. Lithium-ion batteries are part of the lexicon, and parents everywhere are grateful for the 5 min of peace that

portable electronics have occasionally provided us on long journeys.

Stan is a huge presence on campus and has been instrumental in growing our liberal arts university into the R1 institution it is today. I count myself fortunate to be his colleague in the Materials Science and Engineering program and extremely proud to have been part of the North East Center for Chemical Energy Storage (NECCES) that he directs. Stan continues to lead the field he helped develop with important scientific contributions and leadership, most recently developing a fully rechargeable multielectron two lithium battery cathode. In addition, he has trained generations of scientists in the battery community and is a mentor to many more. I have learned a tremendous amount from Stan over the years, from insight into electrochemical reactions to how to navigate university politics. "Stan the Man"-as he is affectionately referred to within NECCES—is a highly deserving Nobel Laureate, and I am thrilled to say that he is at Binghamton University!

Louis Piper, Associate Professor of Physics, Applied Physics & Astronomy

### JOHN GOODENOUGH, AN INSPIRATION TO MANY



Arumugam Manthiram with John Goodenough in 1987 (Photo Courtesy: A. Manthiram)

After obtaining my Ph.D. from the Indian Institute of Technology Madras, I joined John Goodenough's group at the University of Oxford in England in November 1985. Ten months later, I moved with John to The University of Texas at Austin in September 1986. My research work with John was largely on transition-metal oxides, including electrode materials for lithium-ion batteries and high-temperature copper oxide superconductors. On the basis of my Ph.D. dissertation work

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in India on the hydrogen reduction of lanthanide molybdates, such as  $Ln_2(MoO_4)_3$ , I began exploring in 1985 with John a series of  $Fe_2(XO_4)_3$  with X = Mo, W, and S as cathodes for lithium batteries. Surprisingly,  $Fe_2(MoO_4)_3$  and  $Fe_2(WO_4)_3$ displayed a flat discharge potential of 3.0 V vs Li/Li<sup>+</sup>, while  $Fe_2(SO_4)_3$  displayed 3.6 V, although all of them have the same structure with the same  $Fe^{2+/3+}$  redox couple, compared to < 2 V for  $Fe_2O_3$ .<sup>1,2</sup> This is when the drastic shifts in redox energies (inductive effect) depending on the countercation  $X^{n+}$  or the polyanion XO<sub>4</sub> were first recognized. Although then I started exploring phosphates as electrodes, we became fully engaged with copper oxide superconductors in the late 1980s; so I transferred the phosphate work to one of John's Ph.D. students, Geeta Ahuja.<sup>3</sup> On the basis of my initial work with John, 10 years later, the exploration of a variety of phosphates by John's group led to the identification of olivine LiFePO<sub>4</sub> as a potential cathode material for lithium-ion batteries in 1997.<sup>4</sup> My initial work with John has opened up the broad field of polyanion electrodes for both lithium-ion and sodium-ion batteries with a variety of materials with rich structural chemistry and electrochemistry, e.g.,  $LiV_2(PO_4)_3$  and  $Na_3V_2(PO_4)_3$ .

John has introduced the breadth and depth of the fascinating properties of transition-metal oxides to the world. He has been a tremendous force for nearly 7 decades to bridge the chemistry and physics communities while making an exemplary career by uniquely working at the interface between chemistry and physics with specific engineering targets. We admire his passion for science, care for humanity, generosity, and modesty. Those of us who have worked closely with him are grateful for his intellectually stimulating discussions and how he mentors with a lot of love and affection. He has changed the way we think and approach scientific problems. He is inspirational for many, including myself. We wish John well for continued success in science for many more years to come.

Arumugam Manthiram, EAB Member, ACS Energy Letters; Director, Texas Materials Institute, The University of Texas at Austin

### THE PERSON BEHIND THE COMMERCIALIZATION OF LI-ION BATTERIES



Shigeto Okada (R) at a reception party with Prof. Akira Yoshino (L)

All members of the Committee of Battery Technology were pleased to see that Prof. Yoshino's Nobel Prize in Chemistry Award increased the presence of Japan in the battery field. I hope this tailwind will further accelerate and activate the R&D of next-generation post lithium-ion batteries. On behalf of the Battery Technical Committee, Japan, I would like to express my congratulations to the 2019 Chemistry Nobel Laureates Prof. Yoshino, Prof. J. B. Goodenough, and Prof. S. M. Whittingham, pioneers of the lithium-ion battery.

Beginning with the dry battery developed by Yai Sakizo 130 years ago, nickel-cadmium batteries, nickel-metal hydride batteries, and recent sodium-sulfur batteries have been commercialized in Japan for the first time in the world.



Prof. J. B. Goodenough with Dr. Dr. A. K. Padhi (L) and Prof. S. Okada (R) at lunch just after his ECS Olin Palladium Award lecture at 1999 ECS Joint International Meeting in Honolulu (Photo Courtesy: S. Okada)

Even in Japan, which has a long successful R&D history of batteries, the achievements of Prof. Yoshino in the practical application of lithium-ion batteries, especially the four patents relating to (1) Li-ion battery configuration with a  $\text{LiCoO}_2$  cathode and carbonaceous anode (JP Patent No. 1989293), (2) the current shutdown function by a polyethylene microporous membrane (JP Patent No. 2642206), (3) an aluminum current collector (JP Patent No. 2128922), and (4) a battery safety mechanism using a positive temperature coefficient (PTC) device (JP Patent No. 3035677) are noteworthy. Furthermore, it is very impressive that the innovativeness and novelty of these Yoshino patents are now recognized even in academia.

Twenty-eight years ago, the lithium-ion battery commercialized by Sony Energytec Inc. based on these patents of Dr. Yoshino made it possible to downsize and produce lightweight portable digital assistants, and it brought *Ubiquitous innovation*. Now, the lithium-ion battery is further increasing its value as a killer device that directly affects the performance of electric vehicles.

Shigeto Okada, Professor, Kyushu University; Chair, The Committee of Battery Technology, Japan

### "FUN IS CONTAGIOUS"



Saiful Islam (Photo Courtesy: P. Wilkinson)

I suspect most people probably first saw the fantastic Nobel Prize news on a mobile phone, laptop, or tablet computer

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powered by a lithium-ion battery. I'm absolutely delighted that John Goodenough, Stan Whittingham, and Akira Yoshino have been awarded the 2019 Chemistry Nobel Prize. In my view, this award is long overdue, and it is great to see that this important area of materials chemistry has been recognized.

On a personal level, John and Stan have had a major influence on my research over many years from understanding redox processes in spinel oxides to probing Li-ion transport and defects in lithium iron phosphate cathodes. I remember when I was about to give the 2016 Royal Institution Christmas Lectures for BBC TV on the theme of energy (and entitled "Supercharged"), I received a lovely e-mail from John urging me to "have fun with the lectures—fun is contagious". I was very happy to take his advice and I had a lot of fun! Saiful Islam, Professor, University of Bath

# A FEW MEMORABLE MOMENTS WITH STAN WHITTINGHAM AND JOHN GOODENOUGH



With Stanley Whittingham (Top) and John Goodenough (Bottom) (Photo Courtesy: Shirley Meng) I came to know Prof. Stanley Whittingham in 2004, right after I presented my doctoral work at the MRS Fall meeting in Boston. To my surprise, Stan came up to me and nicely asked me a few detailed questions regarding the topic of my talk—layered lithium nickel manganese oxides, designed to replace lithium cobalt oxide as cobalt is too expensive and scarce to be used in electric cars. I noticed that he took very detailed notes about everyone's talks—a habit Stan has that I have always observed. We have collaborated together on new intercalation chemistries since then; Stan is always so supportive of new

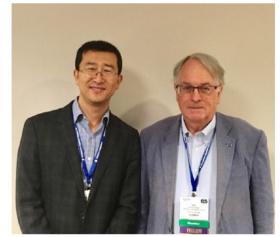
ideas and new approaches. I can see how he is driven by curiosity and truly enjoying the fun of doing science. "I am just a mid-career scientist!" he sometimes jokes, referring to the fact that he is 20 years younger than Prof. John (B. Goodenough).

Prof. John B. Goodenough and I first met in May 2005 at UT Austin, where I had a seminar talk for the very first time. John attended my talk and joined for lunch. He told me he liked the idea of using the first-principles computation method to design materials and to predict and understand their properties—this was such an encouragement to me as some still had serious doubt at that time if computation was ever going to be useful in materials design and discovery. During the 25 year celebration of the lithium-ion battery at the 2016 ECS meeting, at age 94, John came to Hawaii, and hundreds of people took photos with him; I asked him if he was willing to take a selfie with me; John said, "Sure! I think I am still young enough to do that!"

I am so fortunate to have them as my colleagues, mentors, and friends.

Y. Shirley Meng, Professor, NanoEngineering, University of California, San Diego

### CREATING A RECHARGEABLE WORLD



Xiaolin Li with Stanley Whittingham at the 236th Electrochemical Society Meeting in Atlanta (Photo Courtesy: X. Li)

Being a member of the battery community, I am very excited to see the 2019 Nobel Prize in Chemistry finally awarded to John Goodenough, Stanley Whittingham, and Akira Yoshino, a long-overdue recognition. I have known Prof. Goodenough and Prof. Whittingham through their work and professional contacts. To me, they surely won the Nobel Prize for "creating a rechargeable world". Both of them still continue their research on cutting-edge issues and get excited whenever they discuss scientific issues or new battery findings. Their work encouraged me to pursue energy research, and it reiterates Isaac Newton's lifetime reminder "…like a boy playing on the seashore, and diverting myself now and then in finding a smoother pebble or prettier shell than ordinary..."

They are well-respected in the battery research community not only because of their legacy and pioneering footsteps in Liion batteries but also because of their humility. Both John and Stan are very approachable and willing to give suggestions on topics, give feedback on a paper, or serve as mentors to guide the careers of young researchers. John has written an autobiography, "Witness to Grace", that I highly recommend. It is a testament to his humility. My latest contact with Stan

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was at the 236th Electrochemical Society (ECS) meeting in Atlanta, shortly after he became a Nobel Laureate. He could be seen attending the symposia, listening and taking notes during talks that interested him. You would agree with me if you were at the ECS meeting seeing Stan so cooperative, shaking hands and taking pictures with numerous student admirers in the hallway.

I am so happy that I got the chance to share my reflections. Xiaolin Li, EAB Member, ACS Energy Letters

# ILLUMINATING CONVERSATIONS AND DISCUSSIONS



McCloskey Lab photo circa late 2018/early 2019. From left to right: Pedro Arrechea, Tzu-Yang Huang, Eric McShane, Elyse Kedzie, Zachary Konz, Byungchun Park, Bryan McCloskey, Srinivasan Ramakrishnan, Lori Kaufman, Kyle Diederichsen, Helen Bergstrom, Kara Fong, Joseph Papp, David Brown, Elizabeth Corson, Erin Creel, Kristian Knudsen, Matthew Crafton, Davis Perez (Photo Courtesy: B. McCloskey)

Although I have never worked directly with any of the three Liion Nobel Laureates, I am fortunate to have had many interactions with Profs. Goodenough and Whittingham. Among a few other illuminating conversations and seminars, I fondly recall Prof. Goodenough taking time out of his busy schedule to help me prepare for faculty position interviews, even though we had no prior interactions (although I received my Ph.D. at UT Austin, I was in the Chemical Engineering Department working with Benny Freeman on water purification membranes). Benny reached out to Prof. Goodenough during my faculty application process to see if he would be willing to listen to my thoughts for proposed research directions. His feedback was wonderful, and I am grateful to this day for his insight and encouragement. Likewise, I always enjoy my conversations with Prof. Whittingham, which have been numerous over the past decade. Prof. Whittingham's insights on (and critiques of) our Li-air battery work were influential and always appreciated; I look forward to similar discussions whenever our paths cross, which luckily is quite often.

When I speak about Li-ion batteries during my general departmental seminars, I introduce  $\text{Li}^+$  insertion into transition-metal oxide hosts by showing a screenshot of Prof. Goodenough's seminal article describing layered LiCoO<sub>2</sub> (*Mater. Res. Bull.* **1980**, *15*, 783–789). I show Figure 1 of this article, which also contains an image of the LiTiS<sub>2</sub> structure that Prof. Whittingham originally described. I used to comment on my disappointment that neither Profs. Goodenough or Whittingham received the Nobel Prize given their discoveries' obvious societal importance. I am very excited to be able to present their work in its rightful context as Nobel Prize winning during my future seminars! My warmest congratulations to all three of the newest Nobel Laureates. **Bryan D. McCloskey**, EAB Member, *ACS Energy Letters*, Assistant Professor, University of California, Berkeley

FATHER OF MODERN LITHIUM-ION BATTERY (LIB) CATHODES



Yang-Kook Sun (R) with Prof. Goodenough (L), UT Austin Lab

Professor J. B. Goodenough, who recently received the Nobel Prize in chemistry, is the father of modern lithium-ion battery (LIB) cathodes. He was the one to develop all of the existing LIB cathodes (layered LiCoO<sub>2</sub>, spinel LiMn<sub>2</sub>O<sub>4</sub>, and olivine LiFePO<sub>4</sub>), and his research has truly been influential to all of us in the field of LIB cathodes, especially to the research my group has done. On the basis of the LiCoO<sub>2</sub> that Prof. Goodenough developed in 1980, my group has investigated the layered cathodes through the co-precipitation synthesis of LiNiO<sub>2</sub> starting in the late 1990s and expanded to a variety of  $Li[Ni_{1-x-y}Co_xMn_y]O_2$  (NCM) cathodes in the early 2000s, culminating in the development of layered core-shell and gradient NCM cathodes and their incorporation into commercial electrical bikes and vehicles. Furthermore, his other works on LiMn<sub>2</sub>O<sub>4</sub> and LiFePO<sub>4</sub> motivated me to work on enhancing the cycle life of spinel LiMn<sub>2</sub>O<sub>4</sub> through substitution dopants and increasing the tap density and capacity of LiFePO<sub>4</sub> through micron-sized spherical LiFePO<sub>4</sub> particles and LiMnPO<sub>4</sub>-LiFePO<sub>4</sub> core-shell cathodes. All of these works were based on the foundations that Prof. Goodenough set and were only possible because of the novel cathodes he developed.

More impressively, Prof. Goodenough is still active despite his age of 97. I've always heard about his incredible passion for research but was able to first-handedly experience it when I met him in 2016 during the PRiME 2016 meeting and again in November of 2018 at his lab in UT Austin. During the visit, he told me to let others know that he is still active and energetic. The creativity and enthusiasm for his work are always a reminder to the research of my group even today.

Yang-Kook Sun, Senior Editor, ACS Energy Letters; Professor, Hanyang University

# GETTING READY TO CELEBRATE A 100TH BIRTHDAY



Linda Nazar (Photo Courtesy: Linda Nazar)

I've had the great honor-and pleasure-of knowing two of the three Nobel Laurates, John B. Goodenough and Stan Whittingham. Stan was responsible for the first offer I received for a "permanent" position at Schlumberger USA after my postdoc (in fact, I was astonished I received it because I rearended the car of one of the interviewers enroute to a restaurant; Stan must have really stood up on my behalf!). Moving on instead to an academic career, my research has been influenced by Stan in ways too countless to describe over the last 2 decades. I've always relied on his solid support, vigorous intellectual repartee in so many areas of electrochemical energy storage as I served on his Energy Frontiers Center and met him at conferences each year, and enjoyed fierce arguments on topics such as Li-O<sub>2</sub> batteries. I met John Goodenough later in my career, but his seminal work on polyanion battery materials, presented at the ECS meeting in San Antonio TX in 1996, has inspired my research to this day and has extended to many other energy storage materials over the years. John has also been my beacon in solid-state chemistry since I started teaching topics such as magnetism and solid-state ionics, and I have often turned to his and Stan's papers for guidance. I recall giving a rather fundamental science talk at the Florida Battery Meeting around the mid 2000s. The audience was more industrial than academic, so I departed from the stage postpresentation, feeling apprehensive. John stood up as I walked down the aisle, clapped his hand on my shoulder, and said in his characteristically gruff voice, "good stuff!". He saved the day in the best way possible. At a recent workshop at UT Austin to discuss the finer points of solid-state electrolytes and honor John's birthday, I clapped my hand on his shoulder to give him my best birthday wishes. His warm response-that he hoped I'd be there for his 100th birthdaywas classic JBG. I plan on that too.

AN INSPIRATION TO EARLY CAREER RESEARCHERS



At a reception of 2018 Scialog Meeting in Tucson. (L–R, Banerjee, Prieto, Whittingham, and Kamat) (Photo Courtesy: P. Kamat)

When Prof. M. Stanley Whittingham first pioneered the concept of reversible intercalation within solid-state compounds as a means of storing energy in a pathbreaking patent as a young scientist at Exxon in 1977, the world was a very different place! The invention of rechargeable batteries has greatly changed our landscapes and lives. Prof. Whittingham (Stan) epitomizes the power of chemistry to better our lives! He is not just a fantastic scientist but an encouraging mentor and an inspiration for much of our research. He was one of the driving forces in getting Exxon to establish the American Chemical Society ExxonMobil Solid-State Chemistry Faculty Fellowship, which has become somewhat of an institution in solid-state chemistry. As such, it was an incredible honor for me to be nominated by him for this award in 2010 and for him to speak at the award symposium.

I remember asking him a couple of years ago about how his discovery has changed the world, and he replied in his usual humorous manner that he receives many brickbats from faculty colleagues (and even immediate family!) who complain that he is the reason why students no longer pay attention to their lectures, being constantly on their phones or engaged in browsing social media on their laptops. I am often reminded of this comment when teaching freshman chemistry, but of course, his impact goes much beyond the explosive growth of portable electronics, to an unprecedented era of electric vehicles, and potentially paving the way to "Energiewende" the transition to a low-carbon economy.

His toolbox of intercalation reactions, insertion hosts, and electrochemical design rules remains unprecedented and is the foundational basis for an entire discipline and indeed an entire industry. His articles on the functional principles and design of cathode materials have been the guiding blueprints for a field that continues to grow dramatically each year. Perhaps one of my favorite articles is a beautiful piece on chemical lithiation published in the *Journal of Electrochemical Society* that describes in about a page a chemical method for examining Li-ion insertion in potential cathode materials.<sup>5</sup> Earlier this year, when our article on Mg dendrites was published in this journal,<sup>6</sup> Stan drew a clear parallel between lithium and magnesium dendrites and emphasized the need for caution in stating that magnesium batteries are somehow inherently safer.<sup>7</sup> Stan has been a tremendous inspiration to early career researchers across the world, emphasizing a focus on

Linda Nazar, Professor and Canada Research Chair

mechanisms and encouraging the design of new solid-state compounds.

Sarbajit Banerjee, Professor, Texas A&M University; Associate Editor, ACS Omega

# "LET US GO FOR A HIKE"



A selfie moment on the Pima Canyon trail, Tucson, AZ with Stan Whittingham, Venkat Viswanathan, and Yiying Wu (Photo Courtesy: P. Kamat)

That is what Stan Whittingham said last November in Tucson, Arizona while attending the Scialog workshop on Energy Storage organized by the Research Corporation for Science Advancement (RCSA). This intense workshop invites early career scientists and a few experts across disciplines to address frontier topics that are poised for discovery (https://pubs.acs. org/doi/10.1021/acsenergylett.9b00626).

During our free time in the afternoon on the third day, four of us headed to nearby Pima Canyon trail. Of course, as scientists always do, we talked about many scientific stories, failed experiments, and scientific challenges in energy conversion and storage during our 3 h hike along the Pima Canyon trail surrounded by beautiful cacti. Such an outdoor activity is not only refreshing but also provides an opportunity to exchange backstage stories, which are otherwise difficult to capture while in professional settings. Interacting with Stan at these and other scientific meetings remains an inspiration for young and senior researchers. The recognition of the three Nobel Laureates in chemistry this year shows how a simple discovery of a new material in a laboratory decades ago can lead to a transformative technology. Their hard work of tackling energy storage will continue to inspire new generations of scientists years to come.

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### Notes

Views expressed in this energy focus are those of the authors

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