

**Written Testimony of
Daniel Scherson
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Committee on Science, Space, and Technology
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Chairman Weber, Ranking Member Grayson, and Members of the Subcommittee, thank you for the opportunity to testify in today's hearing on Innovation in Solar Fuels, Electricity Storage, and Advanced Materials

My name is Daniel Scherson, and I am the Frank Hovorka Professor of Chemistry and Director of the Ernest B. Yeager Center for Electrochemical Sciences at Case Western Reserve University in Cleveland, OH, and, as of a few days ago President of The Electrochemical Society.

Electrochemistry, a two centuries old discipline responsible for the discovery of several chemical elements, has reemerged in recent years as key to achieve sustainability and improve human welfare. The scientific and technological domain of electrochemistry is very wide, extending from the corrosive effects of weather and other factors, which threatens the safety and integrity of our bridges and roads, to the management of such debilitating ailments as diabetes and Parkinson's disease, and to the development of copper plating processes, which have allowed fabrication of three-dimensional circuitry of ever smaller and more complex architecture. From an even broader perspective, electrochemistry is becoming central to the way in which generate, store and manage electricity derived from such intermittent energy sources as the sun and wind.

Among the most popular and indeed most ubiquitous electrochemical devices ever invented are batteries, which allow chemical energy to be converted into electrical energy. Mostly hidden from sight, batteries are the engines that power our cell phones and other portable electronics, which are critical to the way we communicate and store information. Battery powered cars will also contribute to decrease the release of green-house gases into the atmosphere and thus mitigate their adverse effects on the climate. I have been asked to focus my testimony this morning on aspects of electrochemistry that relate to energy storage, which are

expected to greatly impact, not only the transportation sector, but also, the management and optimization of the electrical grid.

Over the last two decades, the interplay between theory and experiment has experienced a rather radical change in balance. The advent of ever more powerful computers and advanced theoretical methods, have made it possible to predict with increased accuracy the behavior not only of materials, as I am sure will be addressed by my colleagues later in these proceedings, but also of interfaces. The latter play a key role in the chemical industry, where there is growing pressure to develop effective catalysts to increase yields, and lower energy demands. This is also true in the area of electrocatalysts, which are critical to the further optimization of fuel cells, yet another electrochemical device which, like batteries, convert chemical energy into electrical energy. At the pace we have witnessed over this past decade, it would not be surprising that in the next few years, theory will guide the search of new materials. Once identified, it will be up to experimentalists to devise and or implement methods for their synthesis and characterization. Long forgone will be the days of expensive and time consuming testing of compounds in the hope one of them may work. Transportation and the grid account for two thirds of all energy used in the United States. Scientific and technological advancements in these areas will bring about a reduction in operating costs, spur economic growth and create new jobs, and promote US innovation in the global marketplace.

In the area of transportation, any new developments aimed at augmenting reliability, safety and comfort, must be made without compromising performance. Today, batteries for electric cars cannot match already established standards for range per tank of gasoline powered vehicles. In simple terms, the energy a battery can store depends on the charge capacity and its voltage. Whereas the energy is dictated strictly by thermodynamics, the power batteries can deliver is given by the current times the voltage. To illustrate this point, lithium ion battery technology, responsible for the revolution in portable electronics and in transportation, relies on only a single electron per atom of electrode material to store energy and deliver power. Increases in the total energy then require for the size of the battery to be increased, which, in turn, increases the weight of the vehicle and thus the energy required to drive it. While Li-ion batteries have undergone a significant increase in energy density since their introduction in 1991, energy density is currently leveling off. One obvious solution

is to double or, better yet, triple the number of electrons per atom of storage material without decreasing its voltage and thus the energy that can be stored. Among novel chemistries currently being investigated, multi-valent (MV) intercalation is one of the very few that have the potential to supersede the energy density of Li-ion by multiples of two or three. In MV-technology, the Li^+ ion is replaced by a divalent ion such as Mg^{2+} , Zn^{2+} or Ca^{2+} , thereby moving twice the charge per ion transferred between electrodes. Hence, if one can establish that as many Mg^{2+} ions as Li^+ ions can be stored in an electrode material, the charge storage capacity of cathodes per unit volume and weight will be doubled. In addition, Mg-ion technology may enable the use of a Mg metal anode which, with a theoretical capacity of 3800mAh/cc of storage density is among the charge-densest materials imaginable. Combined benefits of a Mg metal anode and a di-valent intercalant cathode are projected to combine to cells with two to three times the energy density of current Li-ion.

While proof of concept of rechargeable Mg batteries has been established, significant hurdles remain for it to become a viable high-energy-density energy storage technology. One of these is to find a suitable cathode material. In an intercalation cathode, ions insert upon discharge, to be released back to the electrolyte and anode upon charge of the battery. In order for charge and discharge to proceed at reasonable rates, diffusion of the MV-ion needs to be fast enough. While such fast diffusion at room temperature is rather common for mono-valent ions such as Li^+ , Na^+ and H^+ , the higher charge of divalent ions makes them interact stronger with the cathode structure and move much slower. Hence, finding good cathode materials among hundreds of thousands of possible compounds is akin to looking for a needle in a haystack. While materials with high MV-ion diffusivity are definitely out there –indeed proof of concept exists– finding them cannot simply be done by trial and error, as each effort to synthesize, test, and characterize a target cathode compound, can take 6-12 months for a research group.

To find high energy density MV-ion cathode materials, the Joint Center for Energy Storage Research (JCESR), which comprises 14 partner institutions led by Argonne National Laboratory is integrating modern computational tools in a high-throughput computational search for the next generation battery materials to predict many of the relevant properties of candidate MV-ion cathode materials, including ion mobility. In such a search, tens of thousands of compounds are run

through a computational screening of successively more challenging property requirements with the objective of identifying a handful of candidate compounds for synthesis and testing. By combining such computational tools with synthesis and electrochemical testing, a more effective search for the next generation battery materials can be achieved.

A challenge to implement a complete high-throughput computational cathode search is that computational methods for predicting the mobility of an ion are extremely slow and computationally unstable. As a result, only “one-at-a-time” investigations are usually performed in theory groups. Developing new methodology that first identifies likely mechanism and migration paths, and then calculates the energy along those paths, has the potential to alleviate this issue to some extent, making a high-throughput search more likely in the future. While there used to be a generic believe that all MV-ion diffusion would be sluggish, the JCESR team has already identified the characteristics of low energy pathways in candidate materials, indicating that under certain conditions, MV diffusion can be more than fast enough for battery application. The key mechanism identified is to search for materials where the MV cation inserts in a coordination that is not its preferred environment (e.g. 4-fold for Mg^{2+} or 6-fold for Zn^{2+}). In such a case, the migration barrier can be kept low if the activated state along the diffusion path has a “better” coordination for the MV ion. An important consequence of this finding is the realization that good materials for one specific MV-ion are more likely than not to be bad for another: e.g. good Zn and good Mg diffusers are barely overlapping materials groups. This strategy has already born fruit in developing a novel cathode material, TiS_2 , with twice the energy density of the Chevrel cathode, the first functioning cathode for Mg batteries. While TiS_2 does not have high enough energy density to surpass Li-ion technology it is an important validation of the search strategy towards even better cathode materials.

Also of importance is the search of new organic electrolytes that will display a large voltage window of stability to allow operation of higher potential electrodes. In particular, most known salts and solvents are incompatible with magnesium metal – causing the formation of a passive layer at the anode surface, and hence blocking reversible magnesium transport. The first working magnesium battery prototype utilized organometallic aluminum chloride, magnesium chloride-based salts which together with a THF solvent made possible a stable

electrolyte between 0-3 V vs magnesium and reversible stripping and plating of a magnesium metal anode. The only other salts that exhibit some promise are halides and borohydrides, in particular the recent carborane salt. However, today, there is no electrolyte that supports both reversible anode operations as well as the large electrochemical window necessary to fulfill the promise of high energy density multivalent energy storage. All magnesium electrolytes with higher anodic stability than 3 V exhibit decomposition reactions at the metal anode. Until recently, there was little fundamental understanding as to why it has been so difficult to find salts and solvent combinations that are stable against magnesium metal and the question of what makes magnesium electrochemistry so different as compared to Li has remained largely unanswered.

To answer this question, the recent revolution in computational materials software and rapidly increasing computing resources is being leveraged. Specifically, efforts at JCESR have led to the development of a rapid and accurate first-principles computational infrastructure for calculating properties of liquid solvent and salt molecules, within the high-throughput infrastructure of the world-leading Department of Energy-funded Materials Project (www.materialsproject.org). The Materials Project was launched at Lawrence Berkeley National Laboratory in 2012, as part of the President's Materials Genome Initiative, and has since calculated the properties of more than 66,000 solids as well as 21,000 molecules. This unique machinery coupled with the supercomputing facilities available at Argonne and Berkeley has made it possible to calculate, and hence screen, hundreds of molecules per week for the set of properties relevant for electrochemical applications. For magnesium electrolytes, electrolyte-relevant properties such as the solvation structure, the electrochemical window, ionic diffusivity etc for a broad range of salts and solvents are being rapidly elucidated. A number of extremely important novel insights were gained by this capability. First, it was learned that almost all multivalent electrolytes, in particular, magnesium-based ones, form contact ion-pairs between the salt cation and anion in organic solvent solutions, even at moderate concentrations. This has fundamental impact on the transport, as well as the charge transfer properties of the electrolyte. The magnesium cations in solution now diffuse together with a negatively charged anion, which reduces the conductivity of the electrolyte and impedes the desolvation process at the anode. Furthermore, the charge transfer process of the magnesium cation at the anode metal interface involves two electrons, which includes a transient, highly reactive

intermediate Mg^+ state, which puts a tremendous chemical ‘pressure’ on the accompanying anion and/or solvent molecules. In most cases, the close proximity of the anion with magnesium during the charge transfer reaction leads to irreversible decomposition of the salt, deposition of decomposition products on the magnesium anode surface and hence loss of active electrolyte. This scenario is fundamentally different from Li electrolytes, where the Li cation is primarily solvated by solvent molecules, and only needs one electron to complete the charge transfer process. The computational screening – and subsequent validation experiments performed within JCESR - confirmed that indeed, borohydrides and halide salts are – so far – the only known salts that are immune to decomposition while delivering and desolvating the magnesium cation at the anode interface. Hence, no

Using the insight of ion-pairing and its impact on the charge transfer process, we leverage our computational capability to uncover which anion or solvent bonds that weaken under the desolvation and charge transfer process. In the computer, we can artificially ‘freeze’ the charge transfer reaction and study the stability of each individual molecular bond of the solvating species, while exposed to the reactive Mg^+ transient cation. The knowledge of what constitutes the weakest links of the salt or solvent molecules allows us to perform target substitutions and modifications; to design in silico new molecules that are inherently more stable under the challenging electrochemical conditions posed by multivalent metal plating. As a result, we have now begun to design completely new salts, some of which are currently being made and tested within JCESR.

From an overall perspective, the problems that remain to be resolved toward achieving sustainability demand a fundamental understanding of the basic processes underlying energy conversion and energy storage at a microscopic level and the development of spectroscopic and structural probes with highly spatial and temporal resolution to monitor individual atomic and molecular events. Such knowledge can only come from new generations of scientists trained at our colleges, Universities and National laboratories, which will require increased research support from the Government.

DANIEL A. SCHERSON
Biography

Daniel Scherson was born in Santiago, Chile in 1951. He received his Licenciatura en Quimica (License in Chemistry) from the Faculty of Sciences, University of Chile in 1974, and later in 1979 a Ph.D. in Chemistry from the University of California, Davis, in the area the non-equilibrium nonlinear thermodynamics under the supervision of Prof. Joel Keizer. After completing his doctoral thesis, he held post-doctoral research appointments in the groups of Prof. John Newman at UC Berkeley, Dr. Phil Ross at the Lawrence Berkeley National Laboratory, Prof. Ernest B. Yeager at Case Western Reserve University and later at the Fritz Haber Institute with Profs. Dieter Kolb and Heinz Gerischer. In 1983, he joined the faculty of the Department of Chemistry at Case Western Reserve University, where he later became the Charles F. Mabery Professor of Research in Chemistry and, subsequently, the Frank Hovorka Professor of Chemistry. He has co-authored over 250 publications and 5 patents in experimental and theoretical areas of electrocatalysis, energy storage and energy conversion, and has advised 26 PhD students.

Over the years he has distinguished himself by combining theoretical principles with novel experimental strategies to develop and/or implement in situ spectroscopic methods covering a wide spectral range from infrared to synchrotron radiation to study, from a very fundamental viewpoint, problems of direct relevance to energy conversion and energy storage. Particularly noteworthy are his contributions in theoretical and experimental aspects of attenuated total reflection IR and UV vis spectroscopies in the presence of convective flow, and applications of synchrotron based techniques and Raman scattering to in situ studies of materials for batteries, fuel cells and supercapacitors, including actual operating devices. His interests also encompass the coupling of ultrahigh vacuum and electrochemical techniques, electrochemistry in ultrahigh vacuum, as well as the implementation of methods for the ultrafast monitoring of surface dynamics at solid electrode-liquid electrolyte interfaces. More recently, he has also become involved in the application of fundamental concepts of physical electrochemistry to the understanding of neural stimulation. Among his many contributions, Prof. Scherson applied in situ reflectance spectroscopy, X-ray absorption fine structure, atomic force microscopy and microgravimetric techniques to elucidate important aspects of the underlying physico-chemical basis of the operation of nickel oxide electrodes in alkaline environments. In addition, his coupling of forced convection techniques and spectroelectrochemistry enabled new insights to be gained into the reduction of sulfur dioxide in aqueous electrolytes. More recently, he pioneered the use of Fourier transform infrared spectroscopy to the study of the reactivity of Li in ultrahigh vacuum environments and, based on the systematic use of this approach, helped unveil the mechanistic pathway of decomposition of linear and cyclic carbonates commonly used as solvents in lithium battery applications. In recent years, Prof. Scherson's attention has been focused on the application of ultrafast techniques for studies of molecular events at electrochemical interfaces, which culminated in the first real time second harmonic generation monitoring of a surface reconstruction induced by the applied potential in the sub-microsecond regime.

He has been deeply involved in the activities of The Electrochemical Society (ECS), serving as Chair of its Physical and Analytical Electrochemistry and Battery Divisions. He was also Associate Editor and later Editor of the Journal of the Electrochemical Society. In recognition to his many scientific achievements he has received a number of prestigious awards including, the Vittorio de Nora-Diamond

Shamrock Postdoctoral Fellowship (1981), Max Planck Gesellschaft Fellowship (1982-83), IBM Faculty Development Award (1983-85), Japan Society for the Promotion of Science Fellowship (1993-94), David C. Grahame Award of the Physical Electrochemistry Division of ECS (2000), Humboldt Senior Fellowship (2002), Faraday Medal of the Electrochemistry Group of the Royal Chemical Society, UK (2004), Japan Society for the Promotion of Science Senior Travel Award (2007), and was made Fellow of the Electrochemical Society (2007).

Over the past few years he has organized a week long Workshop on Electrochemical Measurements sponsored by the Ernest B Yeager Center for Electrochemical Sciences to provide instruction to participants from academia, industry and National laboratories. As part of the Workshop participants have the opportunity to conduct actual experiments with the assistance of graduate students from Case. Lastly, Prof. Scherson is now serving in the Advisory Committees of the Joint Center for Energy Storage Research, (JCESR), led by G. Crabtree at Argonne National Laboratory, (ANL), and of three Energy Frontier Research Centers, (EFRC) led by D. Wesolowski, Oak Ridge National Laboratory, P. Fenter, Argonne National Laboratory, and S. Whittingham, Binghamton, NY.