



**CRITICAL NATIONAL NEED IDEA:
Ultracapacitors Based on Novel Electrode Materials**

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Keywords: electric vehicles, energy storage, ultracapacitors, power density, energy density

I. Introduction

There is a continuing need for alternative energy sources for numerous applications, including automobiles. In the past, ultracapacitors as well as batteries have been developed for many of these applications. However, a majority of work in the energy storage area which is presently being funded by the government is focused primarily on battery development and not on the further development of ultracapacitors which are based on the use of new and unique materials. This philosophy must be viewed with caution, particularly as the batteries show deficiencies in certain areas. The question must be raised as to the fate of many new technologies if batteries are inadequate to meet the requirements of those emerging technologies. Until the advantages of batteries versus ultracapacitors are more clearly defined and measured, it is prudent that major development efforts in both areas continue along similar paths. It is necessary to continue to push ultracapacitor development and that is the focus of this white paper.

II. Background

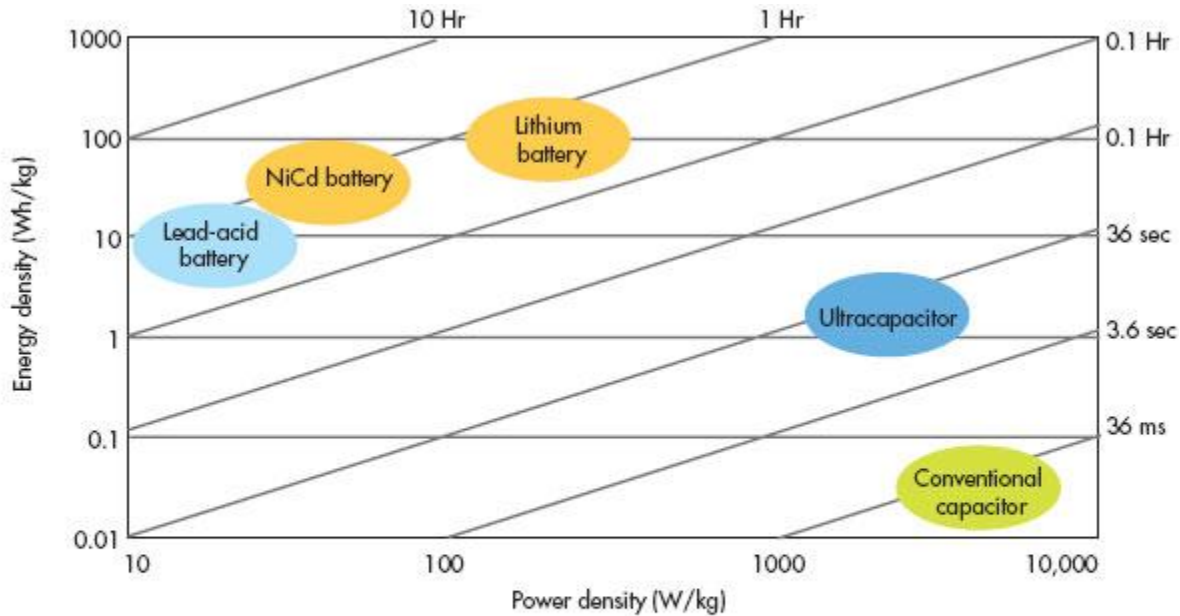
Due to the continuing increase in worldwide gasoline prices, as well as the ongoing public and government pressure for a more environmentally friendly and fuel efficient means of transportation, automotive manufacturers are continuing to develop product lines that incorporate alternatives to the gas-powered drive that is the present hallmark of the industry. Recognizing the need to establish a robust green economy, the American Recovery and Reinvestment Act of 2009 ("Stimulus Bill") has authorized \$16.8 billion in direct spending on renewable energy and energy efficiency programs over the next ten years by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy ("EERE") [1]. Of this \$16.8 billion, the EERE is responsible for \$2 billion for providing funding to manufacturers of advanced batteries and battery system components for energy storage. Among the activities included is the production of lithium ion batteries for use in hybrid electrical systems.

While it is very encouraging that the Stimulus Bill includes funding for the production of lithium ion batteries for use in hybrid electrical vehicle systems, one development that is not mentioned as part of that same Act is the use of ultracapacitor technology in similar energy storage applications. This is very surprising since in 1995 Andrew Burke of the Institute of Transportation Studies at University of California-Davis, a widely recognized expert in the transportation area, published an article on the use of ultracapacitors in electric and hybrid electric vehicles and stated that the development of ultracapacitors for such applications had been underway since the early 1990s [2]. In fact in that same article, Burke proposed that the possible combination of lithium ion and ultracapacitor technology would help accelerate the large scale commercialization of ultracapacitors. Clearly, ultracapacitors have been viewed as offering solutions to many of the energy issues presently before us.

There are differences between ultracapacitors and battery technology which allow for unique benefits to be provided by each type of device. Unlike batteries, which store electricity by chemical means, ultracapacitors store electricity by physically separating positive and negative charges. They accomplish this through the use of two porous plates, or collectors, suspended within an electrolyte, with a voltage applied across the collectors. The applied potential on the positive electrode attracts the negative ions in the electrolyte, while the potential on the negative electrodes attracts the positive ions. A dielectric separator between the two electrodes prevents the charge from moving between the two electrodes.

The figure below, taken directly from Reference [3], shows where ultracapacitors fall in terms of

both power density and energy density compared to other common energy storage devices, such as various types of batteries.



2. A Ragone chart plots storage device energy density versus power density on a log-log coordinate system, with discharge times represented as diagonals. Among other things, it's handy for comparing batteries and ultracapacitors.

As stated in the caption, the graph plots energy density versus power density in a log-log fashion. The figure demonstrates that capacitors, in general, and also, specifically ultracapacitors, offer the advantage of higher power densities compared to other devices. On the other hand, the energy density which is provided by ultracapacitors is lower than with batteries. If the energy density associated with ultracapacitors could be increased, they would offer advantages compared to batteries, including lithium ion batteries.

In specifically comparing some of the other attributes of ultracapacitors to lithium ion batteries, ultracapacitors offer the advantages of being recharged faster and having longer lifetimes. Thus, they offer the possibility of providing large bursts of power for quick acceleration and starting in an automobile. However, the one big disadvantage and one of the main reasons why they have not become more commercially accepted yet is that they store only about 5 % as much energy as a typical lithium ion battery [4].

To understand the reasoning for that limitation, it is necessary to realize that the energy storage capacity in an ultracapacitor is directly proportional to the surface area of the electrodes used in it [5]. Thus, to increase the storage capacity, an increase in the electrode surface area is required. Today, many ultracapacitors use electrode materials made from activated carbons which, due to their porous nature, provide very large surface area. However, the pores in the activated carbon are often irregular in size and shape, thus reducing the efficiency of a large amount of surface area. Thus, in reality, it is not really the surface area measured by common analytical techniques that is important to the utilization and subsequent commercialization of ultracapacitors but the effective or accessible surface area. In fact,

one report [6] states that the actual experimentally determined capacitance, a measure of storage capacity, is only about 10 % of the theoretical value based on surface area data.

In addition to the issue of accessible surface area in existing materials, there is an intrinsic limit to the porosity and hence, surface area which is obtainable with materials presently used, such as activated carbons. An alternative method must be developed to increase the active electrode surface area without increasing the size of the final device. A much more highly efficient electrode for electrical energy storage devices could be realized if the surface area could be significantly increased.

If the storage capacity issue could be resolved, ultracapacitors would offer the advantages to electric vehicles already alluded to and also provide energy storage capabilities similar to lithium ion batteries, thus offering a very attractive alternative to lithium ion batteries for many other developing applications as well. Such an alternative is necessary if lithium ion batteries do not perform satisfactorily in some of these applications. If focus is only directed to lithium ion batteries and there are unresolved issues uncovered, many of the developing technologies could be seriously delayed, thus further adding to the dependence on gasoline and oil as energy sources. This would mean that the environmental issues associated with those energy sources would remain unresolved.

III. Proposed Program

A program in the further development of ultracapacitors which are based on new electrode materials and the associated technology needs to be broad in nature and encompass numerous scientific and engineering disciplines. The initial stages of further development required to meet the storage capacity needs must be focused on additional material development. Both carbon nanotubes [7,8] and graphene [9] have shown quite high surface area values but those values have not always translated directly into increased capacitance values. In both cases, this has been related back to the accessible or effective surface area of the material. The material structure has not been optimized to provide for the highest values possible of the effective electrode surface area.

Thus, one immediate area where much more work is required is in better understanding and tailoring the structure of the electrode material to provide not only a large surface area but a large accessible surface area. Some of that work has already been done with activated carbons [10-12], which are one of the primary materials currently used as ultracapacitor electrode materials but much more study is required to completely define the important parameters which determine the accessible surface area. With graphene, very limited work [9] has been done thus far in correlating the measured capacitance and, hence, ultracapacitor performance, to the measured surface area values. However, recent work [13] has shown that it is possible to vary the surface area of graphene through control of the material production parameters. That approach offers the opportunity to tailor the surface area of the graphene as necessary.

Using the work which has already been done with activated carbons as a guide, measurement techniques for determining the accessible surface area present in graphene materials as a function of different chemistries need to be developed and implemented. Ultimately a correlation between the accessible surface area and the measured capacitance values with these newly developed materials will be obtained. This will require a multi-disciplinary approach, with both aspects of the chemistry of the new materials, such as graphene and carbon nanotubes, being an important part of the work as well as the characterization of the final properties, such as the accessible surface area.

As already stated, an important issue to address is the definition of the most appropriate structure in the electrode material to maximize the capacitance or storage capacity of the ultracapacitor device. In order to address that problem, the development of small scale analytical testing techniques which are based on the use of the actual ultracapacitor electrolyte material in conjunction with the new electrode material will be a key feature of this process. This will lead to effective screening of electrode candidate materials for device production and serve as a time-saving mechanism in that process, allowing for the faster movement of materials to the commercial production stage. Also, the development of these analytical characterization techniques will help guarantee that the proper electrolyte material is being used with each of the new electrode materials. As such, input and guidance from various electrolyte producers and suppliers will be required as part of this program.

Along with the synthesis and characterization aspects of the ultracapacitor development work based on the new electrode materials, a third aspect of the program will be the actual construction and testing of the ultracapacitor devices themselves. For that aspect of the program, the knowledge provided by electrochemical experts is required. People who are very familiar with the details of the construction of the devices are necessary to guarantee that the important relevant factors are addressed. This is necessary to make sure that factors such as test reliability and data reproducibility are addressed in a satisfactory way. The end result needs to be reliable testing data which can be used for the subsequent larger scale mass production of devices which are based on the new materials. Along the way, standard testing protocols will need to be defined so that an easy comparison between new and existing materials can be easily and quickly established.

IV. Impact of Idea on Society

There continues to be a growing level of concern among people at all levels of the country on our continuing dependence on gasoline and oil for the operation of automobiles. A large portion of that concern is driven by the price of gasoline to present levels of about \$3/gallon [14] in many portions of the country. People are finding it increasingly more difficult to pay those prices to drive to and from work. In addition, vacation travel continues to be seriously reduced due in part to the high price of gasoline. This has a serious economic impact on the various businesses that rely on travelers as their main source of income. Further, the effect on the environment of having such a large number of automobiles on the road continues to be a major concern to many. Pollution and its effect on the health and well-being of everyone are critical in that regard.

It is clear that an alternative energy source is needed to address those concerns of the public. The American Recovery and Reinvestment Act of 2009 has begun to address those concerns by providing \$2 billion in grant money to battery manufacturers to further advance lithium ion battery technology. A major concern arises, however, if that technology is not able to adequately address all of the issues which have been raised for alternative energy sources. If that occurs, the country will not have an adequate way to completely address either the oil price issues or the environmental concerns associated with the use of fossil fuels. The \$2 billion allocated to the further development of lithium ion battery technology is a step in the right direction but much more needs to be done. It makes good logical sense to have another technology other than lithium ion batteries readily available to address the problem. Development and further advancement of ultracapacitor technology offers that possibility.

In the past, there have been significant efforts to address ultracapacitor development [15]. Those efforts have met with various levels of success but one of the main concerns is always the fact that the storage capacity cannot meet the energy storage capabilities provided by lithium ion batteries.

That empirical observation has been made but, thus far, very little scientific and technical effort has been made to better understand the reasons for that observation or tailor new materials to overcome the deficiency. The general program which is outlined in this white paper will allow the scientific community to make significant advances in the understanding of the design of materials and provides a unique opportunity in that regard.

The general idea which is presented will provide a means to overcome the energy storage capacity problem which exists with present ultra capacitors and allow for the subsequent mass scale production of ultracapacitor devices which can perform at least at the same level as present lithium ion batteries in all respects. That way, two viable technologies can be moved forward and completely evaluated in the critical area of electric vehicle development. A direct side-by-side comparison can be made on a large scale and relevant conclusions about the advantages and disadvantages of each approach under optimum material conditions can be made. Then, with the data in hand, decisions about which technology to further advance can be made.

If the idea of this white paper is not pursued, only the approach of using lithium ion batteries in alternative energy applications, like electric vehicles, will be addressed. The problem with that approach is that lithium ion battery technology will likely not be applicable to all technologies and, also, there are portions of the electric vehicle technology for which it is not best suited. If that philosophy is followed, the issue arises as to what to do for those applications for which lithium ion technology is not appropriate or does not provide the required results. One immediate consequence would be that all of the developments, both in government and private industry, that are depending on alternative energy sources would be seriously delayed. This could have dramatic effects on not only the environment but also on the overall economy, particularly for industries which have relied on the creation of new jobs in alternative energy areas. To reduce the probability of not having a long-term solution to the energy problem, it would be a very prudent idea to simultaneously pursue more than one approach to tackle some of the issues. The idea which is outlined in this white paper provides the general framework for doing that in the area of ultracapacitors.

Of course, there are other possible alternative energy sources which can be envisioned for certain applications. However, in the case of electric and hybrid vehicles, there is a growing sense of urgency to arrive at a solution quickly. These other alternatives, while offering attractive technical possibilities, often times do not appear to be to have advanced far enough along to be evaluated at a scale appropriate for comparison with either ultracapacitor or lithium ion battery technology. Those two technologies have advanced further and faster than any of the alternatives but there is still much work to be done to completely commercially implement them. Present government funding programs are primarily only addressing the lithium ion battery technology and the omission of the funding of further ultracapacitor development needs to be corrected.

V. Conclusions

It is critical to the future of the country that alternative energy sources continue to be sought and developed. With the ever increasing price of oil and the associated environmental issues of continuing to operate vehicles with gasoline, the need to develop other methods for energy storage is apparent. As evidenced by the fact that the government has provided \$2 billion to the Department of Energy for funding of lithium ion battery manufacturing and development, that need is already well recognized within the present administration.

However, \$2 billion and the focus on lithium ion batteries is just one part of the required development. Battery technology alone will not address all of the applications and concerns which have presented themselves. In order to increase the probability of having viable technologies adequately developed in a short timeframe, other energy storage technologies must continue to be funded as well.

This white paper has recommended that ultracapacitor development which is based on new and developing materials is an area in which additional work and the associated government funding is required. There has already been significant study of ultracapacitors done in the past so there is a large database of information already available. However, as with all new technologies, there are still significant hurdles to overcome before complete commercial success is realized. The most effective way to deal with those obstacles is to use multi-disciplinary teams which span the range of expertise from chemistry and material characterization to the actual producers of the ultracapacitor devices. It is well worth the time and monetary investment associated with overcoming those issues to help guarantee a clean environment for future generations as well as reasonable prices associated with the operation of their vehicles.

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