



Short communication

# High-energy electrode investigation for plug-in hybrid electric vehicles<sup>☆</sup>

Wenquan Lu<sup>\*</sup>, Andrew Jansen, Dennis Dees, Paul Nelson, Nicholas R. Veselka, Gary Henriksen

Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

## ARTICLE INFO

## Article history:

Received 4 August 2010  
 Received in revised form 27 August 2010  
 Accepted 31 August 2010  
 Available online 8 September 2010

## Keywords:

High-energy density electrode  
 Lithium-ion battery  
 Plug-in hybrid electric vehicle

## ABSTRACT

In addition to the development of high-energy density electrode materials for lithium-ion (Li-ion) batteries, other engineering approaches, such as electrode optimization, should be considered in order to meet the energy requirements of plug-in hybrid electric vehicles (PHEV). This work investigates the impact of the electrode thickness on the energy density of (Li-ion) batteries. The impedance results from the hybrid pulse power characterization (HPPC) test indicate that the electrode resistance is inversely proportional to the electrode thickness. This feature makes it possible to use thicker electrodes in (Li-ion) batteries to meet PHEV power requirements. The practical electrode thickness is determined to be around 100  $\mu\text{m}$ , if considering the electrode mechanical integrity when using conventional PVDF binders. Furthermore, cycle performance shows that cells with a higher loading density have a similar capacity retention to cells with a lower loading density.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

The Vehicle Technologies Program within the United States Department of Energy (DOE) called for the development of PHEVs with a 40 mile all-electric range in February 2006 [1]. In fiscal year 2009, DOE focused the efforts of its applied battery R&D program – denoted the Applied Battery Research for Transportation (ABRT) Program – on R&D that would enable achievement of this challenging all-electric range goal. This program assists industrial developers in identifying the major factors responsible for the technical barriers limiting the development of PHEV batteries and in finding viable cost-effective solutions to them. In addition to the calendar life, abuse tolerance, and cost challenges that exist for Li-ion batteries in the HEV application, the issue of providing sufficient energy within the weight and volume requirements became a huge challenge, as did cycle life. In 2008, with historically high gasoline prices up to \$4 gallon<sup>-1</sup> for a period of time, sales of hybrid electric vehicles (HEVs) remained strong. Several automakers announced plans to introduce plug-in hybrid electric vehicles (PHEVs) as well as full electric vehicles (EV).

However, there is no commercially available high-energy material to meet the 40 mile PHEV application established by the

FreedomCAR and Fuels Partnership. High-energy electrode materials research and development became the focus of the ABRT program. Meanwhile, the high-energy battery issue could be addressed by engineering approaches. For instance, electrode porosity and inactive additives have been investigated by both experimental [2] and modeling [3] approaches. The inactive material and loading density of the electrode could be optimized to improve the energy density. Argonne attempted to address this issue from the system level. According to the battery design model developed at Argonne [4,5], thicker electrodes are required in order to meet the goal of PHEV batteries. However, the electrode thickness will affect its integrity, electrochemical performance, and cycleability. In this work, the appropriate and practical thickness of the electrode for high-energy batteries will be investigated. The power capability and cycle life related to the electrode thickness will be discussed.

## 2. Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (Fuji CA1505N, Japan), denoted as NCA, was used as the cathode material in this study. The cathode electrode consists of 82 wt.% active material, 4 wt.% SFG-6 graphite (Timcal) and 4 wt.% C-55 carbon black (Chevron) as conductive additives, using aluminum foil as current collector. The anode material is CGP-G8 graphite, denoted as G8, from ConocoPhillips, USA. The active material in anode consists of 92 wt.%, coated on copper foil. The binder solutions used for the cathode and anode electrode were Keruha #1120 (12 wt.% Poly(vinylidene fluoride) (PVDF) in N-Methyl-2-Pyrrolidone (NMP)) and #9130 (13 wt.% PVDF in NMP), respectively.

<sup>☆</sup> The submitted manuscript has been created by the UChicago Argonne, LLC as Operator of Argonne National Laboratory (“Argonne”) under Contract No. DE-AC02-06CH11357 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

<sup>\*</sup> Corresponding author. Tel.: +1 630 252 3704.

E-mail address: [luw@anl.gov](mailto:luw@anl.gov) (W. Lu).

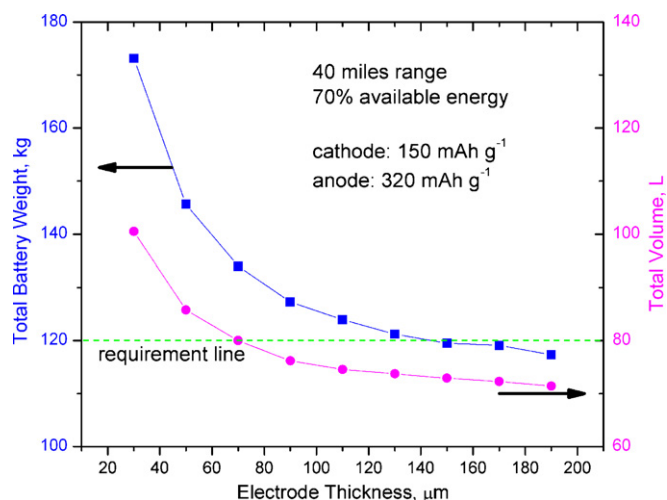


Fig. 1. Total battery weight (kg) and volume (L) as a function of electrode thickness  $\mu\text{m}$ .

A series of cathode and anode electrodes with various thicknesses were prepared using a small laboratory coater built at Argonne. The cathode electrode thickness varies from  $7\ \mu\text{m}$  to  $110\ \mu\text{m}$  with about 32% porosity after the calendaring process [6]. The appropriate thickness anode electrode was selected to match the cathode capacity with capacity ratio of anode to cathode (a/c ratio) ranging from 1.1 to 1.4.

Coin type of cells (20 mm in diameter and 3.2 mm in height—2032) were used in this work to investigate the thickness effect on the electrochemical performance of NCA. Both lithium half cells and full cells were fabricated in an inert atmosphere glove box with an oxygen level of less than 5 ppm. Lithium metal is used as a negative electrode in the half cell, while the G8 graphite electrode is used as the negative electrode in the full-cell configuration. A trilayer film; polypropylene, polyethylene, and polypropylene (Celgard 2325), was used as the separator in both cases. The electrolyte in this work is 1.2 M  $\text{LiPF}_6$  lithium salt in EC/EMC (3/7) solvent.

The electrochemical performance of the coin cells was investigated using the hybrid pulse power characterization (HPPC) profile [7]. From 10% to 90% depth of discharge (DOD), HPPC profiles will be applied to cells at every 10% DOD. During the HPPC pulse, the cell will be pulse discharged at 1.8 C for 10 s followed by a 40 s rest. The cells will then undergo 1.2 C regen pulse for 10 s, immediately followed by C/2 constant current discharge to remove 10% capacity. After a 1 h rest, the HPPC profile will be repeated. From the HPPC test, the area specific impedance (ASI) will be calculated from the voltage difference before and at the end of the discharge/regen pulses. The cycle life of coin cells was determined at room temperature under C/2 rate.

### 3. Results and discussion

Currently, the commercially available electrode materials cannot meet the weight and volume requirements of a 40 mile PHEV. Therefore, it is natural to consider battery structure optimization to improve the battery energy density, for instance, by increasing the electrode thickness. The total battery weight (kg) and volume (L) as a function of electrode thickness  $\mu\text{m}$  (shown in Fig. 1) is calculated using a battery design model developed at Argonne according to PHEV requirements [5]. In this model, the capacity fading is not taken into consideration. It can be seen that the total battery weight and volume decrease with increasing electrode thickness, provided that the specific capacities of NCA and graphite are  $150\ \text{mAh g}^{-1}$  and  $320\ \text{mAh g}^{-1}$ , respectively. Fig. 1 also indicates that the cath-

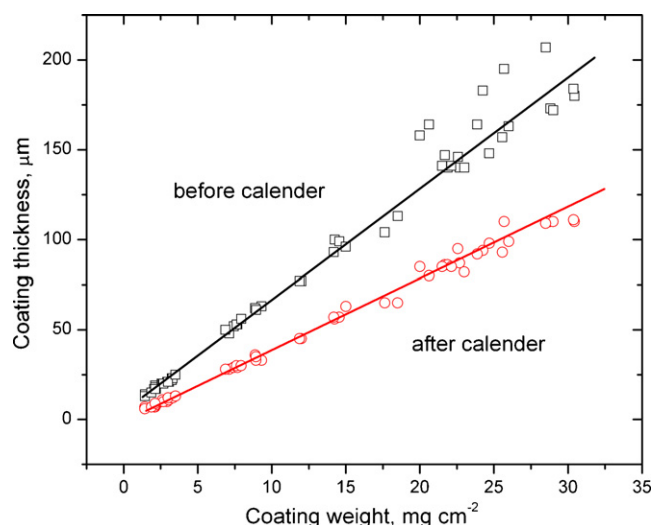


Fig. 2. The relationship between the electrode thickness and coating weight before and after calendaring.

ode electrode should be thicker than  $130\ \mu\text{m}$  if only 70% of the total battery energy will be utilized, which is almost 5 times thicker than that of the NCA cell system for a HEV application. It is also noticed from Fig. 1 that the battery weight reduction rate levels off when the electrode thickness is greater than  $100\ \mu\text{m}$ . This is due to less weight and volume contribution from the current collector and separator with increasing electrode thickness. This limitation makes the high-energy materials research critical for PHEV development in the future.

As discussed previously, a thicker electrode can provide higher energy density for the battery system. However, there is a practical maximum electrode thickness due to mechanical integrity. There is much less energy density improvement of the battery with a further electrode thickness increase under the current electrode configuration. In the lab, the practical electrode thickness for NCA material is determined to be less than  $150\ \mu\text{m}$  after calendaring. Fig. 2 shows the relationship between the electrode thickness and coating weight before and after calendaring. A good linear relationship is obtained for the calendared electrode from low- to high-loading density. However, a non-uniform coating thickness is observed at the high electrode loading region for the electrode before calendaring. It is also noticed that the electrode integrity is getting worse when the electrode thickness is above  $100\ \mu\text{m}$ . The electrode optimization process is needed to develop a thicker electrode to preserve its integrity. For instance, other binders with better binder strength and flexibility are being developed, which allow for thicker electrodes and large volume expansion.

The specific capacity of the NCA electrode with various thicknesses is tested using a Li/NCA half cell and the results are shown in Fig. 3. The deliverable specific capacity of NCA material between 3.0 V and 4.2 V during the first cycle at a C/10 rate decreases slightly with the increasing electrode thickness. The  $7.6\ \text{mg cm}^{-2}$  loading density, indicated by the red arrowhead in the plot in Fig. 3, is equivalent to a  $35\ \mu\text{m}$  coating thickness, corresponding to a Gen2 system. The Gen2 lithium-ion battery system has lithium nickel cobalt aluminum oxide as cathode and MAG 10 graphite as anode, which was developed at Argonne for HEV application [8]. The electrode with  $21.8\ \text{mg cm}^{-2}$  loading density corresponds to  $100\ \mu\text{m}$  coating thickness. The result indicates that the thicker electrode does not affect the usable capacity of the NCA material at a low cycling rate. However, the deliverable capacity is affected by the electrode thickness at a higher discharge rate.

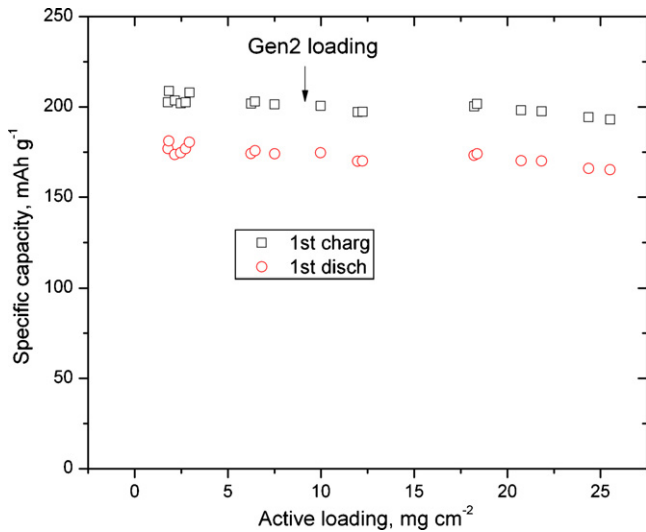


Fig. 3. Results of testing the specific capacity of the NCA electrode with various thicknesses using a Li/NCA half cell.

Fig. 4 shows the relationship between the deliverable capacity and discharge rate of NCA half cells for various electrode loading densities. It can be seen from Fig. 4 that the capacity is not a strong function of discharge rate when the electrode loading is less than  $10 \text{ mg cm}^{-2}$ . When the electrode loading density is larger than  $10 \text{ mg cm}^{-2}$ , the deliverable capacity is still close to the theoretical value with a relatively high discharge rate (less than C/1), which is higher than the depleting rate requirement for a PHEV. However, the usable capacity will drop significantly when the discharge rate increases. For instance, there is only 60% capacity available for the electrode with higher loading density of  $24.4 \text{ mg cm}^{-2}$ .

The power performance of the NCA half cells with various electrode thicknesses was carried out using the HPPC. ASI at 50% DOD of the half cells is plotted as a function of the electrode loading density, shown in Fig. 5. It can be clearly seen that the ASI of the half cells decreases as the electrode thickness increases. This trend levels off when the loading is higher than  $7.5 \text{ mg cm}^{-2}$ . The trend is consistent with theoretical simulations using an electrochemical model [9]. Compared to the model prediction for an NCA electrode, the vertical impedance shift to higher value for the half cell is caused by the interfacial impedance of the lithium electrode, which is set

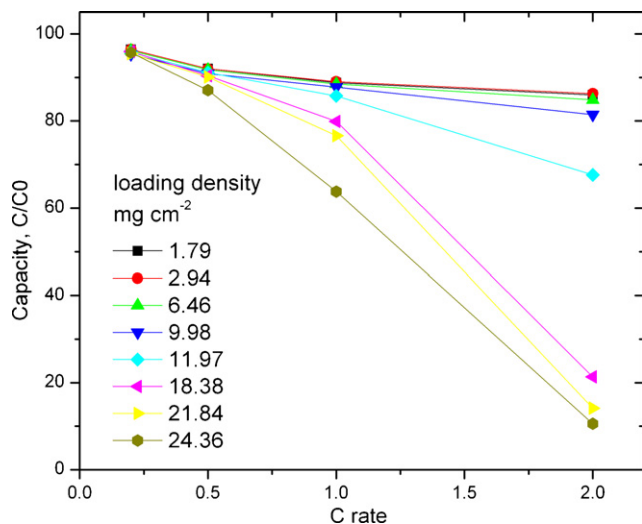


Fig. 4. The relationship between the deliverable capacity and discharge rate of NCA half cells for various electrode loading densities.

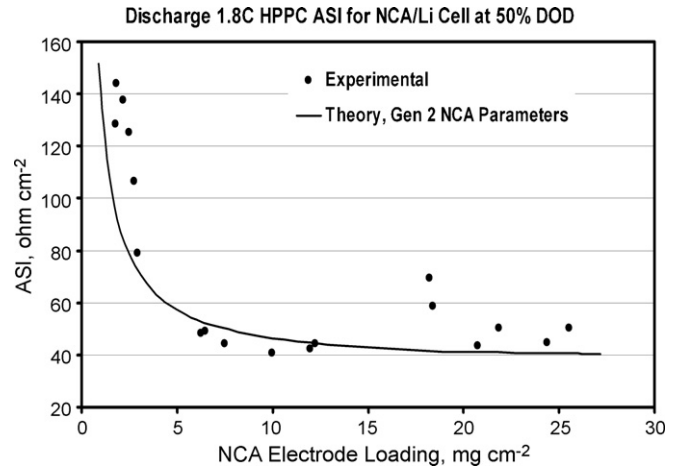


Fig. 5. Area specific impedance (ASI) at 50% DOD of the half cells is plotted as a function of the electrode loading density.

at about  $25 \Omega\text{-cm}^2$  in this fitting. It is also noticed that the rise in impedance at lower electrode loadings from the calculation is consistently higher than the theoretical numbers, which may be associated with the break down of the volume averaging assumption built into the theory (i.e., the thinner electrodes might need to be treated as individual particles rather than averaging out the effects).

Fig. 6 shows the ASI result of G8/NCA full cells tested by HPPC with various electrode thicknesses. Similar to the Li/NCA half cells, the full-cell ASI decreases as the electrode thickness increases. This trend levels off when the electrode loading density is larger than  $7.5 \text{ mg cm}^{-2}$ . However, the overall ASI value of the full cells shifts from  $40 \Omega\text{-cm}^2$  of half cells to lower values,  $20 \Omega\text{-cm}^2$  of full cells. This result indicates that the lithium metal makes a significant contribution to the half-cell impedance. Another issue should be addressed here about the relationship between cell ASI and its rate capability. We noticed that the cell ASI decreases as the electrode thickness increases and levels off according to the results from the half cell and full cell. This does not necessarily mean that the cell with the thicker electrode always has a higher power capability. Assuming a constant C-rate discharge, thicker electrode cells must be discharged at a higher current density, thus tending to offset the lower impedance. The combination of a higher current density

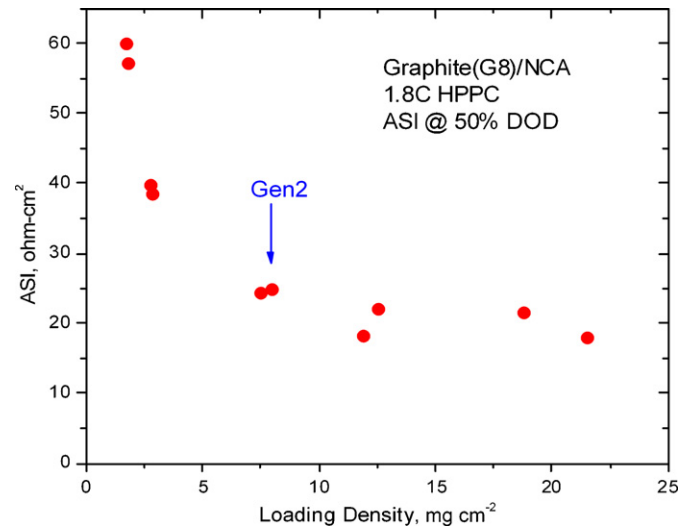


Fig. 6. ASI result of G8/NCA full cells tested by HPPC with various electrode thicknesses.

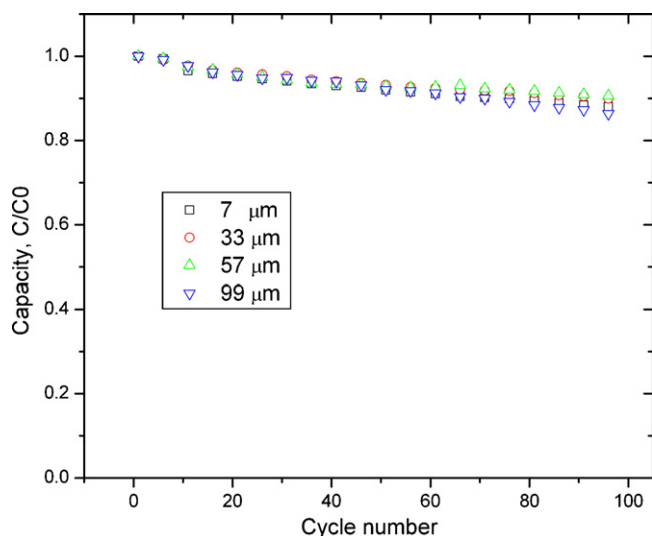


Fig. 7. The normalized capacity fading of cells with various electrode loading densities as a function of cycle number.

and thicker electrode also places more of a strain on the transport of lithium ions in the electrolyte thus possibly limiting its rate capability, as shown in Fig. 4. The complexity of these interactions illustrates the importance of performing full-cell calculations.

The cycleability of the full cells with various electrode loading densities was also tested at the C/2 rate for each cell at room temperature. The C/2 discharge rate is determined from the PHEV goals (11.6 kWh available energy for charge depleting mode at 10 kW rate)[7], when 30% energy margin and 70% of the battery energy usage are taken into account. Fig. 7 shows the normalized capacity fading of cells with various electrode loading densities as a function of cycle number. No obvious difference in terms of capacity fading rate is observed for the full cells with higher electrode loading density under this condition. However, the slightly higher capacity fading rate of the cell with the thickest electrode is noticed in Fig. 7, which is expected. As discussed previously, the very thick electrode has a mechanical integrity issue. This integrity issue will become severe with cycling due to the electrode material volume expansion and contraction. The volume change will not only cause the crack of the particle, but also a thickness change of the laminate [10–12]. The latter one, on one side, might cause the particle

isolation, leading to losing the active site of the electrode materials; on the other side, it might cause an internal short and thermal runaway.

#### 4. Conclusions

None of current commercial available electrode materials has enough energy density to be used in Li-ion batteries to meet 40 mile all-electric range PHEV requirements. An engineering approach was attempted on  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.15}\text{O}_2$  cathode material to improve the energy density of Li-ion batteries by increasing the electrode thickness. Considering the mechanical integrity, the practical electrode thickness is determined to be around 100  $\mu\text{m}$ . The HPPC result indicates that the electrode impedance is inversely proportional to the electrode thickness. This enables good power capability of the Li-ion battery with a higher loading density. Furthermore, the cycle performance shows that the cell with a higher loading density has a similar capacity retention as that with lower loading density.

#### Acknowledgement

Support from David Howell of the U.S. Department of Energy's Office of Vehicle Technologies Program is gratefully acknowledged. Authors would also like to thank Dr. Zhenhua Mao from ConocoPhillips for supplying graphite materials.

#### References

- [1] D. Howell, Annual Progress Report 2008 of Vehicle Technologies Program—Energy Storage Research and Development, 2009.
- [2] H. Zheng, G. Liu, X. Song, V. Battaglia, ECS Transactions 11 (32) (2008) 1–9.
- [3] Y.-H. Chen, C.-W. Wang, G. Liu, X.-Y. Song, V.S. Battaglia, A.M. Sastry, J. Electrochem. Soc. 154 (10) (2007) 978–986.
- [4] P. Nelson, D. Dees, K. Amine, G. Henriksen, J. Power Sources 110 (2002) 349–356.
- [5] P. Nelson, I. Belharouak, K. Amine, G. Henriksen, J. Power Sources 110 (2002) 437–444.
- [6] W. Lu, A. Jansen, D. Dees, G. Henriksen, J. Mater. Res. 25 (8) (2010) 1656–1660.
- [7] Battery Test Manual For Plug-In Hybrid Electric Vehicles, Idaho National Laboratory, 2008 (Version 0).
- [8] D.P. Abraham, J.L. Knuth, D.W. Dees, I. Bloom, J.P. Christophersen, J. Power Sources 170 (2) (2007) 465–475.
- [9] D. Dees, E. Gunen, D. Abraham, A. Jansen, J. Prakash, J. Electrochem. Soc. 155 (8) (2008) A603–A613.
- [10] J. Baker, Electrochim. Acta 45 (1999) 235–242.
- [11] J. Shim, R. Kostecki, T. Richardson, X. Song, K.A. Striebel, J. Power Sources 112 (2002) 222–230.
- [12] J. Christensen, J. Newman, J. Solid State Electrochem. 10 (2006) 293–319.