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Elucidation of Separator Effect on Energy Density of Li-Ion Batteries

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Fast charging of batteries is the key to increase the adoption of electric vehicles. All the components of a battery: anode, cathode, electrolyte and separator, contribute to the limiting factors of fast charging. While majority efforts are focused on novel electrode architecture and electrolyte formulation for high rate capabilities, studies on separators are mostly pertaining to their mechanical and physical properties and little attention has been paid to their effect on rate performance. In this study, we report a comprehensive analysis of the physical properties, electrochemical performance and high rate capabilities of the widely used battery separator Celgard 2325 and Celgard 2500. It is demonstrated that the Celgard 2500 has better electrolyte wettability and $\sim 2 \times$ in electrolyte uptake, and 2.23 Ω/cm^2 less in resistance. Consequently, 57% and 47% improvement in capacity is obtained when charged at 2C and 3C, respectively. This indicates that separator can also play an important role in enabling fast charging for lithium-ion batteries. © The Author(s) 2019. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, http://creativecommons.org/licenses/by-nc-nd/4.0/), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: oa@electrochem.org. [DOI: 10.1149/2.0571914jes]

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Lithium-ion batteries have been one of the front runners for revolutionizing the automobile industry. There still lacks the wide scale adoption of these electric vehicles (EVs) due to the issue of range anxiety and cost. One of the key factors that needs to be addressed for increasing the adoption of EVs to compete with the gasoline vehicles is fast charging. The current U.S. Department of Energy (DOE) goal of fast charging time is less than 15 minutes, while maintaining a cell energy density >200 Wh/kg.^{1–3}

On-going research is mainly focused on novel electrode architecture and formulation of electrolyte to improve the fast charging capabilities as well as to enhance the gravimetric and volumetric energy density for lithium-ion batteries. Ultra-thick electrodes have been fabricated with powder extrusion moulding technology for improving the energy density and enabled high volumetric capacity of up to 340 mAh/cm³ using LTO/LFP chemistry at C/12 c-rate.⁴ Tailored tortuosity in thick electrodes were created via magnetic alignment technique to improve the energy density of the electrodes and achieve high charge rate, i.e. 8 mAh/cm² at 1C.⁵ A combined experimental and modelling study suggested that varying the electrode porosity and negative/positive ratio might not help in improving the fast charging capabilities while enhancing the electrolyte transport properties and reducing the electrode tortuosity were some strategies to achieve the extreme fast charging capabilities.⁶ When replacing traditional LiPF₆ salt with lithium bis(fluorosulfonyl)imide (LFSI), which has higher conductivity and Li-ion transference, it has demonstrated 13% improvement in capacity at 5C with 88% retention after 500 cycles with remaining energy density of ~ 162 Wh/Kg.⁷ Similar work by Dahn and group showed 20% improvement in ionic conductivity at 2C rate by using methyl acetate as a new co-solvent.8-10

While progress in electrode architecture and electrolyte development significantly improved rate capability, further advancement is required to increase the cell energy density, i.e. > 200 Wh/kg, under fast charging.¹¹ Separator is another component in lithium-ion batteries (LIBs) and also plays important roles in determining the rate performance. However, previous studies on separators were mostly pertaining to their mechanical and physical properties and safety.^{12–17} Little attention has been paid to their effect on high rate performance and energy density which are crucial for achieving the DOE goal of extreme fast charging,¹¹ which is elaborated in this work.

A separator, one of the crucial components of a LIB, is a porous membrane which allows ionic transports between the electrodes while isolating the electronic flow.^{18,19} Separators are composed of either nonwoven fabrics or microporous polymers.²⁰ Ceramic layer has been coated to the polymer separator to enhance mechanical strength, thermal stability and electrolyte wettability.^{17,21,22}

One of the important characteristics of a battery separator is that it should be electrochemically stable toward the electrolyte and the electrodes. However, the presence of separator builds on to the electrical resistance in a cell, which negatively affects the battery performance. The resistance in the separator is mainly ascribed to the resistance of electrolyte transport through the porous structure and is a function of the thickness, porosity, tortuosity and surface fraction of pores of the separator. In LIBs, the separator has a considerable influence on the transport of lithium ions.^{23,24} The conductivity and transference number in the electrolyte properties but also the structure of the separator. Studies have shown that ionic conductivity reduces by \sim 5–20% in the pore space compared to the bulk electrolyte conductivity.^{25,26}

Proper selection of a separator is critical for better battery performance that can maximize energy and power density while maintaining required safety feature. Several factors need be considered for selecting the best separator for a particular battery application such as separator thickness, electrolyte uptake, thermal stability, wettability, electrical resistance, porosity, tortuosity, and safety.^{20,23,24} Correlating these properties to the electrochemical performance of the cells at high charge rates is the key to understanding the influence of separators on fast charging and energy density of a cell. Currently, most of the literature is focused on modifying the separators by developing nanoparticle additives and coatings to improve their electrolyte wettability,²¹ mechanical strength and thermal stability.²⁷ The effect of separator on fast charging capability has not been discussed, which is the purpose of this work. Here, we chose two separators with same thickness but various porosities, pore structure to evaluate their effect on both charge and discharge rate performance and cell energy density. The highly porous structure of Celgard 2500 leads to better electrolyte uptake and wettability, lower resistance, and higher rate performance than Celgard 2325 with minimal tradeoff in thermal stability and selfdischarge. The results are applicable to other separators and provide

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Figure 1. SEM images of the surface of Celgard separators: (a) Celgard 2500, (b) Celgard 2325.

guidance in selecting separators for fast charging capability and high energy density. To simply experimental design, a well-known cathode $(\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}]\text{O}_2)$ was chose in this work.^{28,29}

Experimental

As received Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O₂ (NMC532, Toda America), polyvinylidene fluoride (PVDF, Solvay 5130) and carbon black (powder grade, Denka) were used to fabricate the NMC532 cathode using N-Methyl-pyrolidine (NMP) as the solvent and following the procedures reported previously.³⁰ The NMC532 cathode consisted of 90 wt% NMC532, 5 wt% PVDF and 5 wt% carbon black with a mass loading of 27 mg/cm² (3.9 mAh/cm²). The as-coated NMC532 (~55% porosity) was dried at 120°C under vacuum overnight before being assembled into coin cells with Li metal as the counter electrode. One layer of Celgard 2325 or 2500 was used as the separator in each coin cell. Further details of these separators will be provided in the later sections. The coin cells were assembled in an argon filled glove box. The electrolyte was 1.2 M LiPF₆ in EC/EMC (3/7 wt). For the electrochemical testing, the half cells were cycled within a voltage range of 4.2-2.5 V using a potentiostats (VSP, Bio-Logic). The rate performance of the cells was characterized in both charge and discharge. When characterizing discharge capability, the cells were



Figure 2. Contact angle measurements on Celgard 2325 (left) and Celgard 2500 (right) using water and electrolyte.

charged at constant current (C/3, 1C = 160 mA/g) followed by a constant voltage charge at 4.2 V until the current dropped to C/20. Then the cells were discharge at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C. During charge capability evaluation, the cells were charged by constant current at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C without the constant voltage charge step and discharged at C/3. Electrochemical impedance spectroscopy was carried out in a frequency range of 10 mHz to 500 kHz with an amplitude of 5 mV using the VSP potentiostats.

To understand different cell performance with various separators, the separators were characterized by including contact angle (electrolyte wettability), thermal stability, and electrolyte uptake. The contact angle experiment was performed using two different liquids, water and the electrolyte used in the coin cells by a goniometer (Rame-Hart 260-F4). The thermal stability was evaluated by the dimension change of the separators after being heated at different temperatures in air and time durations. The electrolyte uptake was characterized by thoroughly soaking the separators in the electrolyte for one hour. The mass of the separators was measured before and after electrolyte exposure. Electrolyte uptake was presented in mass percentage (%) or volume ratio where the absorbed electrolyte mass was normalized by the mass of separators, and the absorbed electrolyte volume was normalized by the separator volume, respectively. Morphology of the separators was characterized by field emission scanning electron microscope (Zeiss Merlin FE-SEM).

Results and Discussion

Structure and physical properties.—Figures 1a and 1b show the surface SEM images of Celgard 2500 and Celgard 2325 respectively. The Celgard 2500 is mono-layer membrane of polypropylene (PP), while Celgard 2325 is a tri-layer membrane separator with polypropylene-polyethylene-polypropylene (PP|PE|PP) configuration consistent as shown in previous work.³¹ Celgard 2500 has similar structure as Celgard 2325 but is more porous, consistent with the high porosity as shown in Table I.^{20,23,32} The low Gurley number for Celgard 2500 indicates higher permeability.

Both separators have same chemistry (PP) on the surface which is pure dispersive in surface energy (35.3 mN/m).³³ As shown in Figure 2, Celgard 2500 shows more hydrophilic behavior compared to Celgard 2325 with a smaller apparent contact angle with DI-water, which is

Table 1. Properties of separators					
	Thickness (µm)	Porosity (%)	Gurley (s)	PP pore size (nm)	Puncture strength (gf)
Celgard 2500	25	55%	200	28	335
Celgard 2325	25	39%	620	28	>380



Figure 3. Electrolyte uptake for two separators in terms of volume and normalized separator weight.

hydrophilic. Assuming the surface energy of the PP is similar for both separators, the smaller contact angle with DI-water for Celgard 2500 indicates higher apparent surface energy, which is ascribed to the higher porosity (lower surface fraction of PP) and/or lower surface roughness.³⁴ As the electrolyte has a surface tension of 32.2 mN/m with 38.0% polarity,³⁵ the higher apparent surface energy of Celgard 2500 results in smaller contact angle with the electrolyte, indicating better surface wetting as shown in previous work.³⁶

Electrolyte uptake was shown in Figure 3 where the absorbed electrolyte was normalized to the mass and volume of the separators, respectively. Celgard 2500 has almost double electrolyte uptake compared to Celgard 2325 attributing to its high porosity and pore volume, which would facilitate mass transport of lithium ion through the separator.

The thermal stability of the separators plays a significant role on battery safety as high shrinkage may lead to cathodes and anodes uncovered and form short circuit. The thermal shrinkage was measured in terms of the dimensional changes of the separator after being held at different temperatures for 10 and 20 minutes. The dimensional change pertains to the variation in the separator diameter after it is exposed to heat. Both separators show good thermal stability at 120°C with 3.0% and 1.75% shrinkage for Celgard 2500 and 2325, respectively, after 20 min heating. It was noted that the Celgard 2500 tends to fold when exposed to >100°C as shown in Figure 4 but didn't shrink much in dimensions. Heating time also significantly affect the thermal stability. For instance, both separators exhibited higher shrinkage rate when exposed to 100°C for 20 min compared to the 120°C for 10 min.

Electrochemical performance.—The ionic resistance associated with the separator was determined by electrochemical impedance spectroscopy. Both separators were soaked in electrolyte for over 72 hours before being sandwiched between spacers and assembled in a coin cell format. Special caution was paid to minimize additional electrolyte and ensure lithium ions transporting through separator during measurement without bypassing the separator when flooded with electrolyte. Figure 5a shows the Nyquist plots for the cell configuration with all coin cell parts and electrolyte but without separator. The ionic resistance is inidcated by the intercept of the Nyquist curve on the horizontal axis. The resistance through the cell with only spacers is approximately 0.632Ω , while the resistance through the cell with spacer plus electrolyte is 1.26Ω . The increase in resistance is due to



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Figure 4. Thermal stability test for separators. Percentage decrement of the separator diameter at different temperatures and time duration: quantitative (top) and qualitative (bottom).



Figure 5. Nyquist plots for cells with different configuration (a) coin cells plus electrolyte without separator (SS|electrolyte|SS) (b) coin cells with a separator soaked in liquid electrolyte previously (SS|separator|SS).

the inclusion of electrolyte in the cell. Figure 5b shows the Nyquist plot for the two separators with ionic resistance of approximately 7.51 Ω and 12.58 Ω for Celgard 2500 and 2325, respectively. This is equivalent to 2.23 Ω /cm² less resistance due to Celgard 2500 separator. The trends of the ionic resistance match with those reporeted in literature.^{36–38} Based on the ionic resistance, the tortuosities can be computed using the equation shown below,³⁹ which are found to be 2.89 and 3.92 for Celgard 2500 and 2325 repectively. The higher resistance in Celgard 2325 is due to the longer path for lithium ions to cross through the separator. The resistance can be presented in the following equation:

$$R = \frac{d\tau}{\sigma \epsilon A} + R_{contact}$$

where *d* is the separator thickness, τ is the tortuosity, σ is the electrolyte conductivity 9.24×10^{-3} S/cm,⁴⁰ A is the separator area, ϵ is the porosity of separator, and $R_{contact}$ is the contact resistance due to spacers. It is noted that the surface fraction of pores in separator should be used in caculating tortuosity, which could be quite different from the bulk porosity [24]. However, this would require advanced experimental techniques such as FIB SEM Tomography and phase contrast X-ray microscopy coupled with intesive modeling techniques to obtain the tortuosity with the help of 3D image reconstruction.^{25,41,42} Thus, the caculated tortuosity is an approximate value and only for comparasion purpose. The higher tortuosity of Celgard 2325 results in additional 25 μ m diffusion length for lithium ion to shuttel between anode and cathode, resulting to longer lithium ion transport time through the separator. This also suggests that we could either reduce the overall

diffusion length of the cell system by 25 μ m, or increase the electrode thickness equivalent to the diffusion length which could further improve the energy density of the cell.

The effect of separators on rate performance was characterized in half coin cells with two different protocols between 2.5 and 4.2 V. One protocol was to evaluate the discharge rate performance with a constant charge (const CHG) at C/3 (CC) and a trickle current of C/20 while discharged at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C. The other protocol was to gauge the charge rate capability where the cells were discharged (const disCHG) at C/3 while charged at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C. It is noted that there was no constant voltage charge step in this protocol. Figures 6a and 6b show the voltage profiles under constant discharge protocol from coin cells with Celgard 2500 and 2325, respectively. The normalized capacity is the capacity ratio between a particular charge rate and 0.1C. Overall, the cells demonstrated excellent rate performance with \sim 4.0 mAh/cm². There charge capability was pretty identical at low charge rate (e.g. up to 1C) with both separators. However, the cells with 2500 separator demonstrated dramatic improvement, corresponding to 57% and 47% increase over those with 2325 separator when charged at 2C and 3C, respectively. This indicates the separator could play a big role in improving charging capability and energy density. When further increasing the charging rate, the improvement was not significant which is most likely due to the dominant limitation of mass transport in the electrodes. Similarly, the cells with separator 2500 delivered much better discharge rate performance when discharged at 2C to 5C as shown in Figures 6c and 6d. The improvement was approximately 6%, 52%, and 60% for 2C, 3C, and 5C, respectively.

Figures 6e and 6f show the electrochemical performance and capacity retention as a function of charge or discharge rate, respectively. Without the constant voltage charge step, capacity reduced quickly when increasing charging rate. The cells with 2500 separator always demonstrate identical or superior performance to those with 2325 separator regardless cycle protocols. For instance, cells with both separators demonstrated similar discharge capacity (160 mAh/g) at 0.1C. However, the cells with 2500 separator delivered a discharge capacity of 92 mAh/g (~60% capacity retention) compared to the ~60 mAh/g (37% capacity retention) with 2325 separator when charged at 2C. When charged at constant rate (C/3), the discharge capacity was higher especially at high discharge rate indicating significant portion of capacity came from the constant voltage charge step. The cells with 2500 separator still outperformed those with 2325 separator. As shown in Figure 6f, the dicharge capacity retention of the cells with 2500 separator was 82% and 90% compared to the 53% and 82% for those with 2325 separator at 3C and 2C, respectively.

Figures 7a and 7b shows the plot of energy density in electrode level where the total weight of the cathode coating and Al foil was normalized to cell energy. The cells showed very high energy density at low rate due to the high areal loading. Similar to capacity at Figure 6, the cells with 2500 separator offered higher energy density regardless the test protocol. When charged at various rates without a constant voltage step, the cells suffered significant energy loss at high rate (\geq 2C). While the capacity retention was 89% at 2C for the cells with 2500 separator, the energy density retention was only \sim 70%. The lower energy density retention as ascribed to the lower discharged voltage. The gap between charge and discharge energy was also increasing indicating higher polarization which was presented as the different between the average charge and discharge voltage in Figure 8. The voltage difference increased from ~ 0.2 V to > 1 V when increasing charging rate from 0.5C to 5C. The cells with 2325 separator showed even larger polarization, such as 1.25 V at 5C, 0.07 V higher than that with 2500 separator, which is ascribed to the extra 25 µm diffusion length according to the previous discussion. The higher values of voltage difference for 2325 and 2500 separator, 1.25 V and 1.18 V respectively, indicate that cathode and separator also contribute to the limited energy density in fast charging while the graphite anode is considered as the limiting factor.^{11,43} When a constant voltage charge step was included, the voltage difference was much lower showing lower polarization.



Figure 6. Voltage profiles for cells assembled with (a) Celgard 2500 - constant discharge cycle; (b) Celgard 2325 - constant discharge cycle; (c) Celgard 2500 - constant charge cycle; (d) Celgard 2325 - constant charge cycle. Rate performance of NMC532/Li half cells using Celgard 2325 and 2500 separator (e) Discharge capacity in mAh/g. (f) Discharge capacity retention. 'const CHG' indicates constant charge protocol, 'const disCHG' indicates constant discharge protocol.

While rate performance will benefit from higher porosity and/or lower thickness of separator, self-discharge might increase as well. Figure 9 shows the self discharge of the cells after they were charged at C/5 CC to 4.2 V and held at 4.2 V for a total charge time of two hours. The cells with separator 2500 started showing higher voltage drop after 30 h. However, the voltage drop with both separators was not dramatic. At the end of one week rest, the voltage drop was ~60 and 50 mV for 2500 and 2325 separator, respectively.

Conclusions

In this work, the influence of separator on the rate performance and energy density was investigated and were corelated to the separator properties such as electrolyte uptake, contact angle, and porosity. The Celgard 2500 demonstrated better electrolyte wettability and $\sim 2 \times$ in electrolyte uptake, 2.23 Ω/cm^2 less in resistance with minimal penalty in thermal stability and self-discharge. As a result, it enabled superior rate performance, such as 57% and 47%



Figure 7. Energy density (electrode level) at different test protocols: (a) constant discharge cycle; (b) constant charge cycle.



Figure 8. (a) Average voltage profiles at different charge rates for constant discharge protocol. (b) Average voltage profiles at different charge rates for constant charge protocol.



Figure 9. Self discharge of the cells in terms of voltage vs time, after charging the cells to 4.2 V and allowing them to rest for 168 hours.

improvement when charged at 2C and 3C respectively. This study provides important insights on the fast charging aspect of lithium ion batteries from the viewpoint of separator properties. It was also noted that the effect of highly porous separators on battery safety needs further investigation.

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