Diffusion-Limited C-Rate: A Fundamental Principle Quantifying the Intrinsic Limits of Li-Ion Batteries

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The critical challenge for the user acceptance of electric vehicles is the simultaneous improvement of the driving range and fast charging capabilities, which are related to the energy and power density of the storage device. Lithium-ion batteries (LIBs) are currently the most promising candidate to push electric vehicles toward the mass market. However, they suffer from a tradeoff between energy and power density, forbidding arbitrary combinations of high storage capacity and fast charging capability. Herein, a simple electrochemical principle describing the intrinsic limits of LIBs is reported. It is deduced that the tradeoff between energy and power density originates from diffusion limitations in the electrolyte. The electrochemical approach of diffusion-limited current density is adapted to porous Li-ion insertion electrodes, resulting in the “diffusion-limited C-rate” (DLC). The theoretical considerations are in excellent agreement with experimentally observed rate limitations of a large number of electrodes with different active materials and varying design parameters. While the C-rate drawn from an LIB cannot be higher than the DLC without significant capacity decline, parameter variations that improve the DLC reduce the nominal specific capacity. This relationship makes the DLC a fundamental quantity revealing the most expedient optimization approaches and promising directions for future battery research and development.

Li-ion batteries (LIBs) were continuously improved over the last decades, aiming at longer operating times of mobile electronic devices and mass implementation in high-energy applications, such as all-electric or hybrid-electric vehicles.[1–4] However, owing to safety concerns, range limitations, and inadequate fast-charging capability, the user acceptance for automotive applications is still quite limited.[5–7] Several approaches were carried out to improve the energy density at the cell level, such as the development of high capacity anode[8,9] and cathode[10,11] materials, improvements of the electrode design[12,13] and composition[14–16] as well as optimization of the cell architecture.[17,18] Moreover, researchers analyzed the rate limiting factors of electrodes for LIBs in great detail to understand the complex charge transport and transfer reaction processes and optimize materials and cell components accordingly.[19] It has been found that the rate performance can be improved by increasing solid-state diffusivity,[20] conductive additive type and content,[21] or electrode porosity,[22] by the optimization of electrolyte properties, such as concentration,[23] and viscosity,[24] and by decreasing the particle size of active materials[13,25] and the electrode thickness.[26–28] Although these measures lead to a gradual improvement of decisive performance metrics, a tradeoff between energy and power density became obvious, forbidding arbitrary combinations of high storage capacity and fast charging capability. Understanding this tradeoff and the accompanied practical limits of LIBs is critical for their further improvement and the development of “beyond Li” battery technologies.

Herein, we present a simple but powerful electrochemical principle describing the tradeoff between storage capacity and rate capability of electrodes for LIBs. Such electrodes are porous composites consisting of particles of the active storage material, binder and conductive additives coated on a metallic current collector foil. The pores are filled with a liquid electrolyte containing Li-ions as charge carriers. The specific capacity (energy density equivalent) of such an electrode is given by the specific capacity of the active material and its share in the electrode.

Figure 1 illustrates the sensitivity of the specific capacity to the most decisive electrode parameters using a typical LiNi1/3Mn1/3Co1/3O2 (NMC111)-based cathode as the baseline (see Section S3 in the Supporting Information for details on the computations). Please note that here the specific capacity of the electrode also includes the masses of conductive additives, binder, current collector and the pore electrolyte, which is often ignored in the literature but has significant impact on the energy density (see Section S2 in the Supporting Information for details). It turns out that some electrode properties hardly affect the energy density, such as the porosity, the conductive additive and binder content, and the particle size (cf. Figure 1).
Accordingly, these electrode properties can be optimized with respect to the rate capability without significant losses in energy density. For example, the conductive additive content can be increased until limitations of the electron transport in the composite become negligible. Similarly, the particle size of the active materials can be reduced to avoid any significant \( \text{Li}^{+} \) diffusion limitations in the solid phase (short diffusion pathways) and charge transfer limitations at the solid/electrolyte interface (large specific surface area). In contrast to that, the electrode thickness and the specific capacity of the active material cannot be optimized regarding the rate performance without affecting the energy density. Although, increasing the electrode thickness significantly enhances the specific capacity of the electrode up to approximately 100 \( \mu \text{m} \), theoretical\cite{19,29–34} and experimental\cite{35–38} results clearly show that large electrode thicknesses lead to low rate capability originating from \( \text{Li}^{+} \) diffusion limitations in the electrolyte. Similarly, increasing the gravimetric capacity of the active material enhances the specific capacity of the electrode, but the larger current density at a given C-rate also leads to increased \( \text{Li}^{+} \) diffusion limitations in the electrolyte and a corresponding decline in capacity at higher rates.

From these theoretical considerations, it can be concluded that the tradeoff between energy and power density originates from \( \text{Li}^{+} \) diffusion limitations in the pore electrolyte, as sketched in Figure 2. During discharging, \( \text{Li}^{+} \) are extracted from the anode material and inserted at the cathode side. Accordingly, the \( \text{Li}^{+} \) concentration, \( c_{\text{Li}^{+}} \), in the electrolyte increases at the anode side and decreases inside the porous cathode, forming a concentration gradient throughout the cell. Although no stationary state establishes during operation of a porous insertion electrode, the magnitude of the \( \text{Li}^{+} \) concentration gradient depends on the applied current and the effective transport properties of the porous structure. Enhancing the current increases the concentration gradient. For a particular current, the \( \text{Li}^{+} \) concentration close to the cathode current collector decreases to zero (Figure 2d). This current is defined as the diffusion-limited current density, \( j_{\text{lim}} \), of the porous electrode. It can be computed based on a combination of Fick’s and Faraday’s laws and considering the electrode design parameters by\cite{39}

\[
j_{\text{lim}} = \frac{2zF D_{\text{eff}} c_{\text{Li}^{+}}^0}{L}
\]  

In Equation (1), \( z \), \( F \), \( c_{\text{Li}^{+}}^0 \), and \( L \) are the valence, the Faraday constant, the initial \( \text{Li}^{+} \) concentration in the electrolyte, and the thickness of the electrode layer, respectively. The effective diffusivity in the porous structure, \( D_{\text{eff}} \), can be estimated using the Bruggeman approximation,\cite{40} which correlates the tortuosity factor, \( \gamma \), of porous media with porosity, \( \varepsilon \)

\[
D_{\text{eff}} = D \varepsilon^{\gamma}
\]  

While \( j_{\text{lim}} \) states the diffusion-limited current density (e.g., in units of mA cm\(^{-2}\)), charge and discharge currents of batteries are typically given in terms of the so called “C-rate,” which specifies the inverse time needed to charge or discharge the battery at the given current. For instance, C-rates of 0.1 and 2.0 h\(^{-1}\) define currents capable to charge the cell in 10 and 0.5 h, respectively, depending on the actual capacity. To combine the concepts of diffusion-limited current density and C-rate, we introduce the “diffusion-limited C-rate” (DLC), which

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**Figure 1.** Nominal specific capacity of a composite electrode for varying a) electrode thickness, b) porosity, c) specific capacity of the active material, d) conductive additive content, e) binder content, and f) particle size (see Section S3 in the Supporting Information for details on the computations).

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**Figure 2.** Nominal specific capacity of a composite electrode for varying a) electrode thickness, b) porosity, c) specific capacity of the active material, d) conductive additive content, e) binder content, and f) particle size (see Section S3 in the Supporting Information for details on the computations).
is defined by the ratio of $j_{\text{lim}}$ and the nominal areal capacity of the electrode, $Q_{\text{areal}}$, and can be written as

$$\text{DLC} = \frac{j_{\text{lim}}}{Q_{\text{areal}}} = \frac{2zFDE\varepsilon c_{\text{Li}}^{\varepsilon}}{\omega_{\text{AM}} \rho Q_{\text{inAM}} L_e (1 - \varepsilon)}$$

(3)

with $Q_{\text{inAM}}$, $\omega_{\text{AM}}$, and $\rho$ being the gravimetric capacity, the mass fraction of the active material and the apparent density of the composite, respectively (see Section S2 in the Supporting Information for details). If the C-rate applied to the electrode is higher than the DLC, a significant Li$^+$ depletion will take place inside the porous cathode during discharging (cf. Figure 2e,f) and in the anode during charging. The sections of the electrode, where the Li$^+$ concentration tends to zero, cannot contribute to the electrode reaction anymore. Consequently, exceeding of the DLC results in a massive reduction of the attainable capacity.

Figure 3 shows DLCs of typical LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NCM111)-based cathodes plotted against the electrode thickness and the corresponding areal capacity (Figure 3a), and the specific capacity of the electrode (Figure 3b) (see Section S3 in the Supporting Information for details). The DLC decreases significantly with increasing electrode thickness, due to the
extended diffusion length. According to these correlations, the DLC of electrodes with large specific capacity, as it is required for high-energy applications, is significantly reduced, prohibiting fast charging capability and attesting the empirically well-known tradeoff between energy and power density.

To prove the validity of the DLC principle, porous insertion electrodes with different active materials and design parameters were fabricated and analyzed regarding their rate performance (see Section S1 in the Supporting Information for details). Figure 4a shows the DLCs of Li$_4$Ti$_5$O$_12$ (LTO)-based anodes plotted against the corresponding areal capacity. As expected, the DLC clearly decreases with increasing areal capacity and thickness of the electrodes, respectively. Figure 4b depicts results of the rate capability tests. Significant differences in the rate performance are observed for the different electrodes, depending on the thickness and porosity. In Figure 4c, the attained relative capacity is plotted against the ratio of the applied C-rate and the DLC of the respective electrode. In this case, the rate capabilities of the cells are almost identical, indicating that the DLC is the underlying mechanism that limits the rate performance. If the applied C-rate is smaller than the DLC, the attainable capacity is close to the nominal value. Exceeding the DLC results in a dramatic reduction of the attainable capacity due to the reasons described above.

Slight deviations from this behavior are observed for thin electrodes. In this case, other rate limiting factors become dominating, as will be discussed below. Similar results are observed for a number of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (NCM111)-based cathodes with different electrode design parameters (Figure 4d–f). Again, the rate performance significantly depends on the thickness and the porosity of the electrodes (Figure 4e), whereby the capacity starts to drop after exceeding the corresponding DLC (Figure 4f). Indeed, we could not find any electrode in our database or in the literature that not exhibits dramatic capacity losses at rates higher than the respective DLC (see Section S4 in the Supporting Information for additional data). Consequently, despite its simplicity, the DLC is an accurate and universal indicator for the rate capability of porous insertion electrodes for LIBs. Of course, electrodes not designed properly might show significant capacity decline before reaching the DLC because additional factors can influence the rate performance, such as charge transfer kinetics, diffusion of Li$^+$ in the active materials and the ohmic resistance of the composite. Therefore, the DLC not describes the rate performance of any electrode but states the optimal rate performance for the given active material and electrode design. In other words, the C-rate drawn from an LIB cannot be higher than the DLC without a significant decline in attainable capacity, making the DLC a fundamental quantity of a porous insertion electrode that can be used straightforward to reveal the most expedient optimization approaches.

The theoretical and experimental results indicate that the fast charging capabilities of LIBs can be improved by decreasing the electrode thickness or increasing the porosity. While this is indeed true, it does not benefit the goals of modern high-energy applications, such as all-electric or hybrid-electric vehicles. Reducing the electrode thickness, to meet a predefined rate performance, dramatically deteriorates the mass ratio of active to inactive materials. Similarly, increasing the porosity benefits the effective transport properties of the electrode, improving the rate performance but decreasing the energy density due to both, the lowering of the active material content and the enhancement of the electrolyte mass that is contained in the pores. According to these examples, it is clear that distinct interdependencies exist between the DLC, representing insuperable limits of the rate performance, and the energy density of the cell.

Figure 5 shows the nominal specific capacity of composite electrodes plotted against the respective DLC, representing the rate performance limit, for varying electrode and material
properties (see Section S3 in the Supporting Information for details on the computations). Increasing the gravimetric capacity of the active material is by far the most expedient approach to increase both the specific capacity of the electrode and the rate performance (Figure 5a). The higher the gravimetric capacity of the active material is, the thinner the electrode can be designed to reach the same specific capacity while leading to an enhanced DLC due to the quadratic dependence on the electrode thickness (cf. Equation (3)).

Increasing the porosity, which correlates with a decrease of the electrode density, lowers the specific capacity for low rate applications but becomes beneficial for high rate applications (Figure 5b). Therefore, the optimal porosity design depends on the desired application and required rate performance, respectively.\(^{41}\) Similarly, the tortuosity factor \((\gamma)\) of the composite has significant impact on the effective transport properties of the electrode.\(^{41}\) Lowering the tortuosity improves the high rate performance while preserving the specific capacity (Figure 5c). First approaches of designing low tortuosity electrodes for LIBs were recently developed,\(^{42,43}\) showing promising results and confirming the optimization potentials predicted by the DLC principle. Increasing of the Li\(^+\) concentration and diffusion coefficient of the electrolyte increases the DLC and allows thicker and less porous electrodes, which benefits the specific capacity for high rate applications (Figure 5d,e). However, optimizing these quantities is nontrivial due to complex interdependencies with the battery chemistry, such as SEI formation, and electrochemical stability range, and the electrolyte properties, such as conductivity. Recent research on high concentrated\(^{28}\) and low viscosity\(^{44}\) electrolytes shows considerable improvements of the rate performance, confirming the optimization potentials predicted by the DLC principle. Interestingly, the thickness of the current collector also exhibits a significant optimization potential regarding high rate applications (Figure 5f). At a first glance, this appears counterintuitive because the current collector does not affect the DLC. However, electrodes with a thin current collector can have thinner active material layers while preserving their specific capacity. The porosity of such an electrode can be reduced until the transport properties match the desired DLC, which increases the amount of active material and simultaneously reduces the pore electrolyte. This means that the reduction of the current collector thickness not just simply improves the mass ratio of active to inactive materials but also allows more favorable design parameters resulting in a disproportional increase of the specific capacity of the electrode.

We want to underline again that the capacity-DLC data in Figure 5 represent the intrinsic limits of the electrode performance, since the DLC cannot be exceeded without significant capacity decline (cf. Figure 4). To keep our statements as general as possible, we use specific capacity and DLC instead for other cell chemistries employing liquid electrolytes, such as Na-ion batteries, Li–sulfur batteries, and dual-ion batteries. Specific attention should be paid for materials that undergo a significant volume expansion during operation. In this case, the DLC principle has to be modified by the introduction of a volume expansion factor, correlating any dynamic changes...
of the porosity and the thickness (swelling) with the state of charge of the electrode (see Section S5 in the Supporting Information for details). Considering volume expansion effects leads to an state of charge dependence of the DLC according to the changes of porosity and thickness of the electrode. Consequently, the rate performance prediction for materials that undergo significant volume changes is more complex when compared to intercalation materials with negligible volume expansion, necessitating further investigations. Nevertheless, it is clear that the fundamental insights gained from the DLC principle are also valid in the case of such materials.

The DLC principle can also be applied to evaluate experimental results, such as rate capability tests (cf. Figure 4). If the capacity of the electrode or battery cell decreases significantly for rates lower than the DLC, the rate capability is not restricted by the intrinsic diffusion limitations in the electrolyte but by other factors, such as the ohmic or SEI resistance, the rate constant of the electrode reactions, or the diffusivity of Li ions in the active materials, which can be optimized by improving composition or design with only slight impact on the energy density (cf. Figure 1).

In summary, we report a fundamental principle describing intrinsic performance limits of secondary batteries. It is shown that the empirically well-known tradeoff between energy and power density of LIBs originates from Li\(^+\) diffusion limitations in the electrolyte, forbidding arbitrary combinations of high specific storage capacity and fast charging capabilities. The DLC principle accurately reflects experimentally observed rate limitations of a large number of porous insertion electrodes with varying active materials and design parameters. While the C-rate drawn from an LIB cannot exceed the DLC without significant capacity losses, parameter variations that improve the DLC affect the nominal specific capacity in opposite direction, leading to an inherent tradeoff between energy and power density. We believe that, despite its simplicity, the DLC principle can be highly valuable for understanding and improving the practical limits of secondary batteries, leading the way for future battery research and development. Based on the current insights, the development of high capacity and high voltage cathode materials are by far the most expedient optimizing approaches at the cell level.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was supported by the German federal Ministry of Education and Research (BMBF) (Grant No. 03XP0070B). Marco Fritsch, Nils Junker, Jann Seeba, and Sebastian Reuber (Fraunhofer IKTS Dresden) are gratefully acknowledged for the preparation of the electrodes and fruitful discussions.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

energy density, fast charging, Li-ion batteries, power density, tradeoff

Received: August 2, 2019
Revised: October 22, 2019
Published online: November 25, 2019

[1] B. Scrosati, J. Garche, *J. Power Sources* **2010**, 195, 2419.
[2] Y. Etacheri, R. Marom, Y. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **2011**, 4, 3243.
[3] B. Scrosati, J. Hassoun, Y.-K. Sun, *Energy Environ. Sci.* **2011**, 4, 3287.
[4] J.-M. Tarascon, M. Armand, *Nature* **2001**, 414, 359.
[5] D. Andre, S.-J. Kim, P. Lamp, S. F. Lux, F. Maglia, O. Paschos, B. Stiasny, *J. Mater. Chem. A* **2015**, 3, 6709.
[6] R. Schmuch, R. Wagner, G. Hörpel, T. Placke, M. Winter, *Nature Energy* **2018**, 3, 267.
[7] Y. Ding, Z. P. Cano, A. Yu, J. Lu, Z. Chen, *Electrochem. Energy Rev.* **2019**, 2, 1.
[8] S. Goriparti, E. Miele, F. de Angelis, E. Di Fabrizio, R. Proietti Zaccaria, C. Capiglia, *J. Power Sources* **2014**, 257, 421.
[9] W.-J. Zhang, *J. Power Sources* **2011**, 196, 13.
[10] N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, 18, 252.
[11] R. Marom, S. F. Amalraj, N. Leifer, D. Jacob, D. Aurbach, *J. Mater. Chem. 2011*, 21, 9938.
[12] S. De, P. W. C. Northrop, V. Ramadesigan, V. R. Subramanian, *J. Power Sources* **2013**, 227, 161.
[13] J. Ye, A. C. Baumgaertel, Y. M. Wang, J. Biener, M. M. Biener, *ACS Nano* **2015**, 9, 2194.
[14] C. Heubner, T. Liebmann, M. Schneider, A. Michaelis, *Electrochim. Acta* **2018**, 269, 745.
[15] S. Luo, K. Wang, J. Wang, K. Jiang, Q. Li, S. Fan, *Adv. Mater.* **2012**, 24, 2294.
[16] G. Liu, S. Xun, N. Vukmirovic, X. Song, P. Olalde-Velasco, H. Zheng, V. S. Battaglia, L. Wang, W. Yang, *Adv. Mater.* **2011**, 23, 4679.
[17] M. Roberts, P. Johns, J. Owen, D. Brandell, K. Edstrom, G. El Enany, C. Guery, D. Golodnitsky, M. Lacey, C. Lecoeur, H. Mazor, E. Peled, E. Perre, M. M. Shaijumon, P. Simon, P.-L. Taberna, *J. Mater. Chem. 2011*, 21, 9876.
[18] T. S. Arthur, D. J. Bates, N. Cirigliano, D. C. Johnson, P. Malati, J. M. Mosby, E. Perre, M. T. Rawls, A. L. Prieto, B. Dunn, *MRS Bull.* **2011**, 36, S23.
[19] R. Tian, S.-H. Park, P. J. King, G. Cunningham, J. Coelho, V. Nicolosi, J. N. Coleman, *Nat. Commun.* **2019**, 10, 1933.
[20] W. Du, A. Gupta, X. Zhang, A. M. Sastry, W. Shyy, *Int. J. Heat Mass Transf.* **2010**, 53, 3552.
[21] B. Zhang, Y. Yu, Y. Liu, Z.-D. Huang, Y.-b. He, J.-K. Kim, *Nanoscale* **2013**, 5, 2100.
[22] W. Bauer, D. Nötzel, W. Wenzel, H. Nirschl, *J. Power Sources* **2015**, 288, 359.
[23] Y. Yamada, A. Yamada, *J. Electrochem. Soc.* **2015**, 162, A2406.
[24] Y. W. Denis, K. Donoue, T. Inoue, M. Fujimoto, S. Fujitani, *J. Electrochem. Soc.* **2006**, 153, A835.
[25] L. Xue, X. Li, Y. Liao, L. Xing, M. Xu, W. Li, *J. Solid State Electrochem.* **2015**, 19, 569.
[26] M. Doyle, J. Newman, A. S. Gozdz, C. N. Schmutz, J.-M. Tarascon, *J. Electrochem. Soc.* **1996**, 143, 1890.
[27] R. Zhao, J. Liu, J. Gu, *Appl. Energy* **2015**, 139, 220.
[28] H. Zheng, J. Li, X. Song, G. Liu, V. S. Battaglia, *Electrochim. Acta* **2012**, 71, 258.
[29] T. Danner, M. Singh, S. Hein, J. Kaiser, H. Hahn, A. Latz, J. Power Sources 2016, 334, 191.
[30] N. Besnard, A. Etiemble, T. Douillard, O. Dubrunfaut, P. Tran-Van, L. Gautier, S. Franger, J.-C. Badot, E. Maire, B. Lestriez, Adv. Energy Mater. 2017, 7, 1602239.
[31] F. Jiang, P. Peng, Sci. Rep. 2016, 6, 32639.
[32] Z. Du, D. L. Wood, C. Daniel, S. Kelnaus, J. Li, J. Appl. Electrochem. 2017, 47, 405.
[33] K. G. Gallagher, S. E. Trask, C. Bauer, T. Woehrle, S. F. Lux, M. Tschech, P. Lamp, B. J. Polzin, S. Ha, B. Long, Q. Wu, W. Lu, D. W. Dees, A. N. Jansen, J. Electrochem. Soc. 2016, 163, A138.
[34] W. Mei, H. Chen, J. Sun, Q. Wang, Sustainable Energy Fuels 2019, 3, 148.
[35] C. Heubner, A. Nickol, J. Seeba, S. Reuber, N. Junker, M. Wolter, M. Schneider, A. Michaelis, J. Power Sources 2019, 419, 119.
[36] H. Gao, Q. Wu, Y. Hu, J. P. Zheng, K. Amine, Z. Chen, J. Phys. Chem. Lett. 2018, 9, 5100.
[37] C. Heubner, J. Seeba, T. Liebmann, A. Nickol, S. Börner, M. Fritsch, K. Nikolowski, M. Wolter, M. Schneider, A. Michaelis, J. Power Sources 2018, 380, 83.
[38] X. Zhang, T. W. Verhallen, F. Labohm, M. Wagemaker, Adv. Energy Mater. 2015, 5, 1500498.
[39] P. M. Biesheuvel, M. Z. Bazant, Phys. Rev. E 2010, 81, 31502.
[40] D.-W. Chung, M. Ebner, D. R. Ely, V. Wood, R. Edwin García, Modell. Simul. Mater. Sci. Eng. 2013, 21, 074009.
[41] H. Li, Y. Tao, X. Zheng, J. Luo, F. Kang, H.-M. Cheng, Q.-H. Yang, Energy Environ. Sci. 2016, 9, 3135.
[42] J. S. Sander, R. M. Erb, L. Li, A. Gurijala, Y.-M. Chiang, Nat. Energy 2016, 1, 3828.
[43] B. Delattre, R. Amin, J. Sander, J. de Coninck, A. P. Tomsia, Y.-M. Chiang, J. Electrochem. Soc. 2018, 165, A388.
[44] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, A. Yamada, J. Am. Chem. Soc. 2014, 136, 5039.
[45] J. Wang, Y. Yamada, K. Sodeyama, C. H. Chiang, Y. Tateyama, A. Yamada, Nat. Commun. 2016, 7, 12032.