



Practical relevance of charge transfer resistance at the Li metal electrode|electrolyte interface in batteries?

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Abstract

The theoretically possible energy and power densities of rechargeable batteries are practically limited by resistances as these lead to overvoltages, particularly pronounced at kinetically harsher conditions, i.e., high currents and/or low temperature. Charge transfer resistance (R_{ct}), being a major type of resistance alongside with Ohmic (R_{Ω}) and mass transport (R_{mt}), is related with the activation hindrance of electrochemical reactions. Its practical relevance is discussed within this work via analyzing Li | Li cells with the galvanostatic/constant current (CC) technique. R_{ct} at Li|electrolyte interfaces is shown to be relevantly impacted by electrode–electrolyte interphases; implying the electrolyte type, as well. While solid polymer electrolytes (SPEs), e.g., based on poly(ethylene) oxide (PEO), show negligible R_{ct} , it is evident for commercial liquid electrolytes and readily increase during storage. Given the asymptotic overvoltage vs. current behavior of R_{ct} , obeying Butler-Volmer equation, R_{ct} gets less relevant at enhanced currents, as experimentally validated, finally pointing to the dominance of R_{Ω} and (depending on system) R_{mt} in the overall resistance.

Keywords Resistance · Charge transfer · Overvoltage · Li metal battery · Liquid electrolyte · Solid polymer electrolyte · Butler-Volmer · Fast charge

Introduction

The battery outcome in terms of e.g., energy/power density is practically limited by Ohmic- (R_{Ω}), charge transfer- (R_{ct}) and mass transport (R_{mt}) resistances. They induce overvoltages and decrease the discharge voltage as well as the accessible capacity, especially at kinetically harsher conditions, i.e., high current rates and/or low temperature [1–6]. Rating the practical relevance of R_{Ω} , R_{ct} , and R_{mt} , can be vital for systematic battery R&D and can be easily investigated during battery operation, i.e., during constant current (CC) cycling via analysis of overvoltages as illustrated in Fig. 1 [2, 7].

At low current excitation, all resistance types behave linear and the respective overall resistance can be calculated according to Ohm's law [5]. At high currents, the effective R_{ct} becomes smaller as a result of an asymptotic voltage vs. current relation, obeying the Butler-Volmer equation, as shown in Fig. 1 (right-hand sight, red curve) [2, 5]. Though, the respective resistances are literature well-known and can be easily obtained via e.g., electrochemical impedance spectroscopy (EIS), their application-relevance is hardly discussed, in particular at application-relevant currents, as these are usually by orders of magnitude higher than the excitation currents applied in EIS. Besides the in-depth complexity of the Butler-Volmer equation which contains various system-specific constants, e.g., symmetry factor and exchange current density [8, 9], and which can be also expressed by the Tafel-plot [10] for the discussion of this work, the asymptotic voltage-current relation is predominantly relevant. In this context, the literature already points to possible overestimation of R_{ct} due to its absence in Li metal batteries (LMB) at the Li interphases formed with ceramic-based solid electrolytes (SE) [2, 11–14].

Here, simple CC-technique-based experiments [2, 7] are highlighted to systematically evaluate the relevance of R_{ct}

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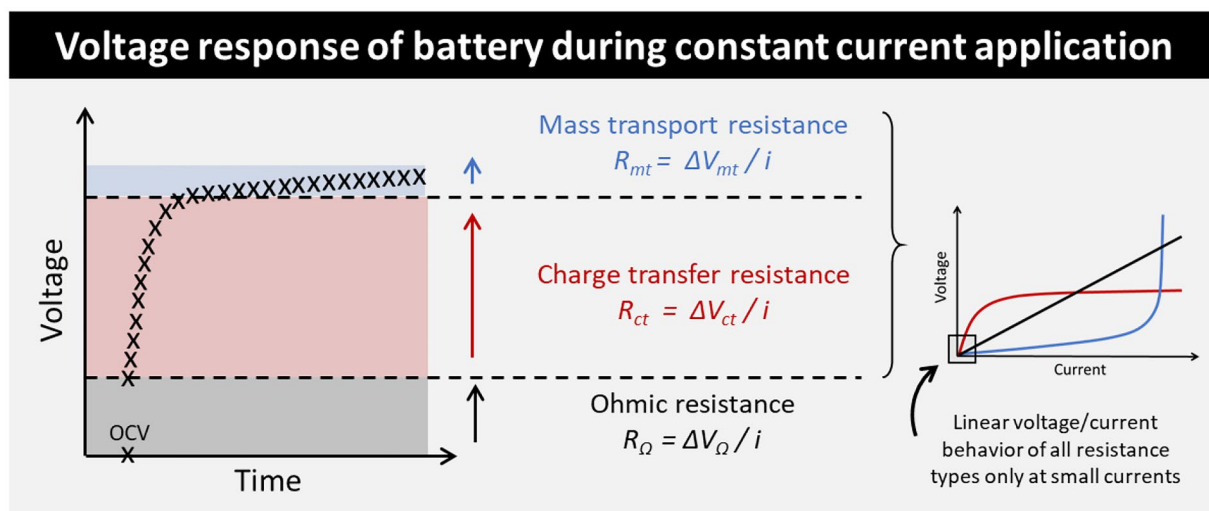


Fig. 1 Schematic illustration of a voltage–time plot during a constant current application showing a chronological order of resistances, i.e., beginning with Ohmic- (R_{Ω}), immediately followed by charge transfer- (R_{ct}) and mass transport resistance (R_{mt}). At small currents the

resistances behave linearly (= can be considered constant) and can be simply distinguished and calculated, while at high currents R_{ct} and R_{mt} get dynamic and deviate from constant behavior

at Li metal electrode/electrolyte interfaces for both, liquid electrolyte (LE), and SE at currents beyond the frequently used in EIS in order to get an application-oriented picture.

Results and discussion

At small constant current (CC), the respective cell resistances, i.e., Ohmic- (R_{Ω}), charge transfer- (R_{ct}) and mass transport resistance (R_{mt}) display a linear overvoltage/current behavior (Fig. 1) and can be calculated via Ohm's law, as shown in Fig. 2 [2, 7, 15]. The initial voltage drop, i.e.,

the difference between open circuit voltage (OCV) and the first experimentally derived resistance data point, corresponds to R_{Ω} and amounts to $45 \Omega \text{ cm}^2$ and $124 \Omega \text{ cm}^2$ for a liquid- (LE) and a solid electrolyte (SE)-based Li || Li cell, respectively (Fig. 2a, b). The R_{ct} and R_{mt} can be distinguished on the basis of their characteristic overvoltage vs. time profiles [2]. While the overvoltage due to R_{ct} builds up logarithmically, thus is particularly pronounced after current onset, R_{mt} -induced overvoltage gets pronounced after a characteristic duration (Sand's time). In LE-based cells R_{mt} is negligible due to fast ion transport within the standard electrolyte (here, 1 M LiPF₆ in ethylene carbonate (EC):

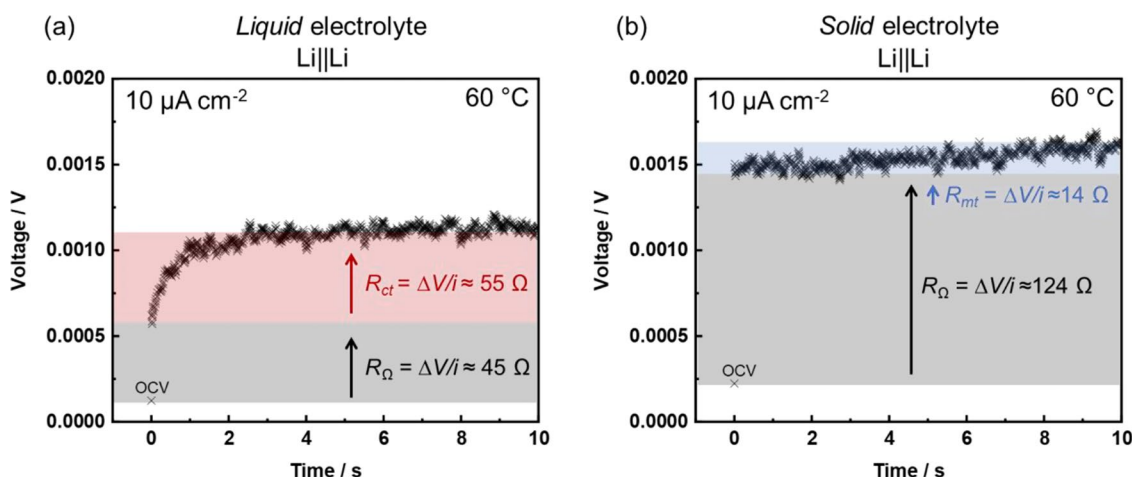


Fig. 2 Voltage vs. time plots from CC measurements, comparing LE (a) and SE (b) in symmetric Li || Li cells at 60 °C, measured after 24 h. Both cells show R_{Ω} , while R_{ct} and R_{mt} -induced characteristic overvoltages are solely observed in LE- and SE-based cells, respectively

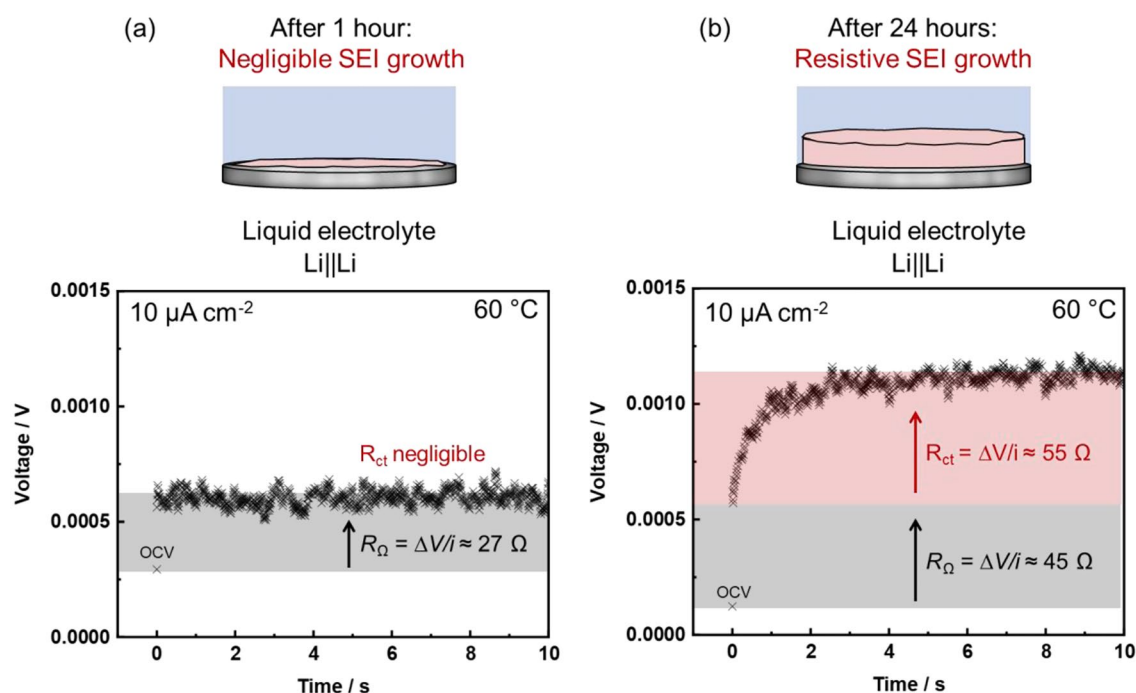


Fig. 3 Voltage vs. time behavior of LE-based Li || Li cells at 60 °C, after storage of **a** 1 h and **b** 24 h. The initial absence and progressive growth of R_{ct} suggests a relation with a progressive SEI change

ethyl methyl carbonate (EMC); 3:7 by wt.), as depicted in Fig. 2a [3]. In contrast, a typical linear increase of overvoltage caused by R_{mt} can be seen in Fig. 2b for the lower-conducting poly(ethyleneoxide) (PEO)-based electrolyte with 1 M LiTFSI [16–18].

The R_{ct} is only observed in the LE-based cell (Fig. 2a), in line with literature [2, 11–14] and can be related with different properties of the solidelectrolyte interphase (SEI) on Li metal [19–22]. It might be attributed to a higher rate of surface exchange at the electrode/electrolyte interface, possibly driven by higher Brownian motion and diffusion, and finally resulting in enhanced electrolyte consumption and a thicker SEI.

The dependence of R_{ct} from the SEI nature is validated by varying storage time of Li || Li cells at 60 °C, as shown in Fig. 3. Interestingly, also the LE-based cell has no R_{ct} initially (after 1 h), but gets more pronounced after 24 h ($55 \Omega \text{ cm}^2$) and is even higher than R_{Ω} ($45 \Omega \text{ cm}^2$). In general, a longer storage time can be related with a thicker/more resistive SEI [19–21, 23–25] and increases both R_{Ω} and R_{ct} , i.e., transport resistance through SEI and activation barrier, respectively [19].

For reasons of linearity between current and voltage, the applied current densities of $10 \mu\text{A cm}^{-2}$ are rather low

compared to application currents (see Fig. 1). Practical areal capacities of battery cells range between 2 and 3 mAh cm^{-2} [26–28] and correspond to current densities of 4–6 mA cm^{-2} , when aiming at fast charge rates of e.g., 2C. The asymptotic voltage-current relation of the Butler-Volmer equation *theoretically* suggests lower R_{ct} at elevated currents, as mentioned in the “Introduction” and, indeed, can be *experimentally* validated, as shown in Fig. 4.

The increase in current density from 10 to 100 $\mu\text{A cm}^{-2}$ and finally to 1000 $\mu\text{A cm}^{-2}$ (Fig. 4a–c), leads to a decrease in R_{ct} from $55 \Omega \text{ cm}^2$ to $38 \Omega \text{ cm}^2$ to finally $12 \Omega \text{ cm}^2$, respectively, while R_{Ω} remains almost constant ($45\text{--}46 \Omega \text{ cm}^2$), which is in line to linear (Ohmic) current-overvoltage relation, as schematically illustrated in Fig. 4d. From a practical point of view, higher applied currents than 1000 $\mu\text{A cm}^{-2}$ are experimentally not reasonable in these cells as these relative harsh currents can likely affect Li surface morphology and additionally affect overvoltage [29]; which might be related with wavering voltage response in Fig. 4c. Nevertheless, the decrease in R_{ct} can still be experimentally validated for application-relevant currents ($< 1 \text{ mA cm}^{-2}$), finally proving decreased relevance of this resistance contribution for faster charge [11], while enhanced contribution of R_{Ω} ; and in the case of SEs additionally R_{mt} can be observed [4].

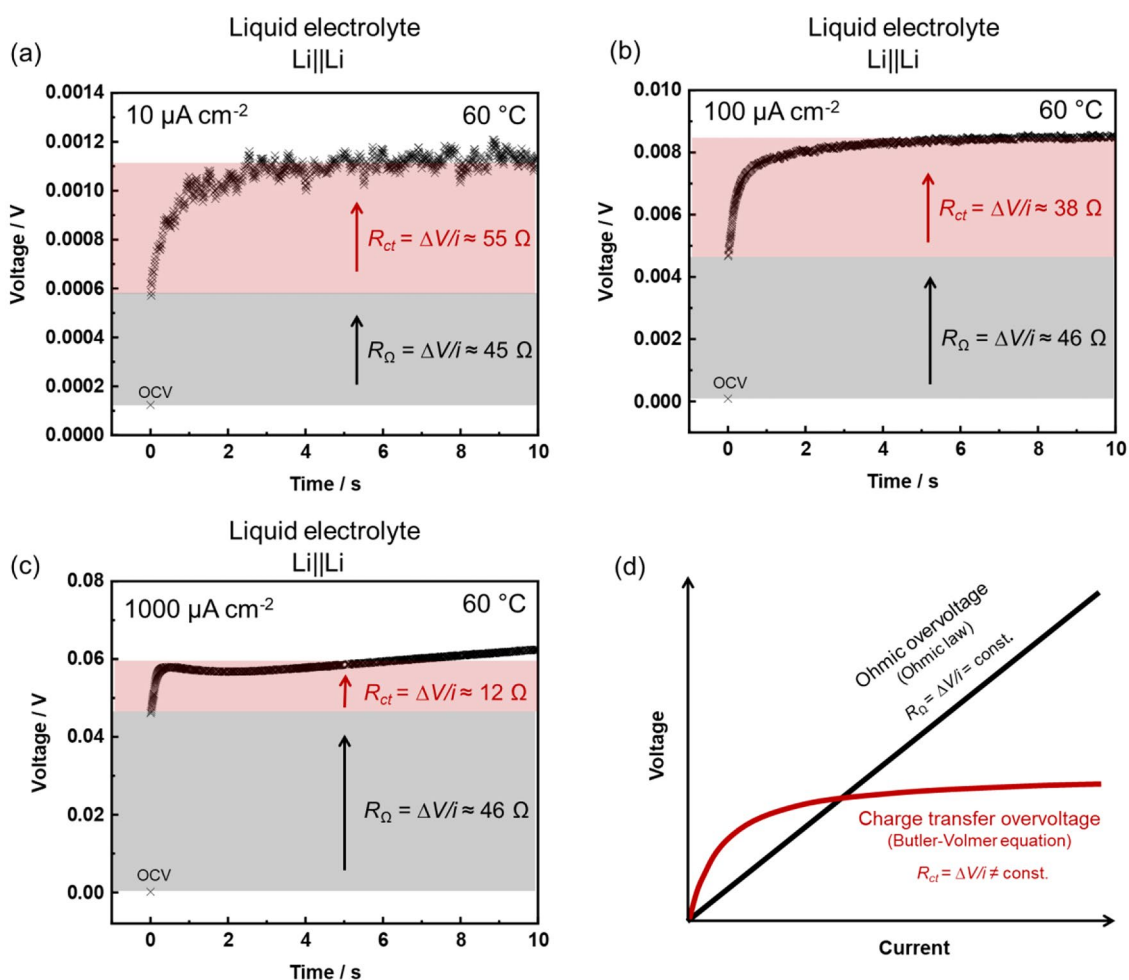
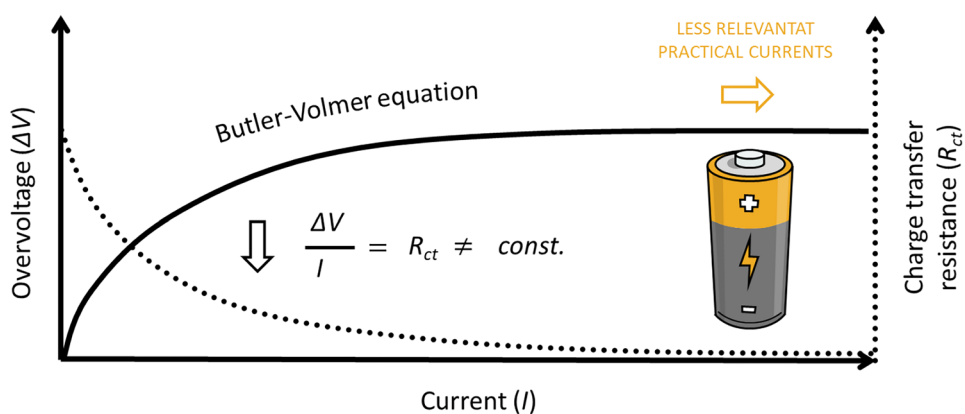


Fig. 4 Voltage vs. time plots of LE-based Li || Li cells at 60 °C with varying current densities, **a** $10 \mu\text{A cm}^{-2}$, **b** $100 \mu\text{A cm}^{-2}$, and **c** $1000 \mu\text{A cm}^{-2}$. R_{ct} decreases with increased current density, while R_Ω

remains almost constant, **d** which is in line with their characteristic voltage-current relations

Fig. 5 Schematic overview of the overvoltage development, described by Butler-Volmer equation, and the accompanied charge transfer resistance as a function of current. Charge transfer resistance is relevant at low currents (almost linear overvoltage-current relation), while its relevance decreases with increased currents



Conclusion

Charge-transfer resistance (R_{ct}) that can be described with the Butler-Volmer equation is a major resistance type in electrochemical storage devices alongside with ohmic (R_{Ω}) and mass-transport (R_{mt}) resistances. Frequently observed via electrochemical impedance spectroscopy (low excitation currents), their practical relevance is discussed in this work for application-relevant higher and galvanostatic currents within Li | | Li cells [8, 19, 30]. Major differences in terms of the type of electrolyte (liquid vs. solid) are shown. R_{ct} is basically absent for a polymer-based *solid* polymer electrolyte, while it progressively grows in contact with a conventional *liquid*-electrolyte (LE). Absence of R_{ct} for solid electrolytes (SEs) is in line with previous literature, observed for ceramic-based SEs ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, LLZO) [11–13].

Given the asymptotic voltage vs. current relation of the Butler-Volmer Equation, R_{ct} becomes less distinctive at elevated currents and is experimentally validated via increasing current densities; while the Ohmic resistance remains constant in the course of its linear voltage vs. current relationship [3]. Ohmic resistance can be concluded to make a major contribution to the total cell resistance at elevated currents (e.g., under fast charge conditions). In addition, for dual-ion conducting solids, the relevance of R_{mt} will increase with higher currents, as well, as shown in the literature [31].

Electrochemical impedance spectroscopy [32, 33] is, indeed, a sensible method to determine R_{ct} , but in the course of the typically applied low excitation currents, it can lead to overestimation of R_{ct} for real-life batteries.

Consequently, R_{ct} can be interpreted as an activation hindrance of an electrochemical reaction at the electrode/electrolyte interface, and its relevance is affected by the nature of interphases and the type of electrolyte [19], and/or the magnitude of the applied currents [4] (Fig. 5).

While Li | | Li cells are reasonable as a model system to investigate charge transfer for varied electrolyte systems, e.g., LEs and SEs, the impact of R_{ct} in practical cell setup and conditions, e.g., composite electrodes and high applied currents, require further in-depth investigations.

Experimental

(a) Materials

Poly(ethyleneoxide) (PEO, MW 300.000 Da), 99.5% was purchased from Sigma-Aldrich, Germany. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.9%) was purchased from Solvay, France. Lithium metal (Albemarle) was purchased from Albemarle, USA. Glass fiber paper (Whatman) was purchased from VWR, Germany. Lithium hexafluorophosphate (LiPF_6) of 1 M in

ethylene carbonate (EC):ethyl methyl carbonate (EMC) 3:7 (by weight) “LP57” was purchased by BASF, Germany. Material storage and sample preparations were performed in a dry-room with a dew point of $-65\text{ }^{\circ}\text{C}$. PEO was dried under vacuum of 10^{-7} mbar at $45\text{ }^{\circ}\text{C}$ and LiTFSI at $110\text{ }^{\circ}\text{C}$ for 2 days before use. Whatman glass fiber paper was punched in discs (16-mm diameter) and dried at $100\text{ }^{\circ}\text{C}$ under vacuum.

(b) SPE membrane preparation

PEO-based SPE polymer membranes were prepared by dry mixing PEO and LiTFSI with a molar ratio of 20:1 (EO:Li). The obtained mixture was stored in a pouch bag under vacuum overnight ($60\text{ }^{\circ}\text{C}$). The resulting gum-like material was sandwiched between Mylar foil sheets and pressed at $100\text{ }^{\circ}\text{C}$ with an applied pressure of 15 bar for 10 min.

(c) Cell assembly

Symmetric Li | | Li cells (two-electrode coin cell configuration) were assembled using polymer membranes and/or glass fiber separators (+ 200 μL liquid electrolyte) with 16-mm diameter, sandwiched between lithium metal electrodes (15-mm diameter).

(d) Electrochemical measurements

Constant current experiments were conducted on an Arbin Instruments battery cell test system at $60\text{ }^{\circ}\text{C}$ in a climate chamber (Mettler). The used current densities are mentioned in the figure captions.

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References

1. Winter M, Brodd RJ (2004) Chem Rev 104:4245–4269
2. Stolz L, Gaberšček M, Winter M, Kasnatscheew J (2022) Chem Mater 34:10272–10278
3. Kasnatscheew J, Rodehorst U, Streipert B, Wiemers-Meyer S, Jakelski R, Wagner R, Laskovic IC, Winter M (2016) J Electrochem Soc 163:A2943–A2950

4. Weiss M, Ruess R, Kasnatscheew J, Levartovsky Y, Levy NR, Minnmann P, Stolz L, Waldmann T, Wohlfahrt-Mehrens M, Aurbach D, Winter M, Ein-Eli Y, Janek J (2021) *Adv Energy Mater* 11:2101126. <https://doi.org/10.1002/aenm.202101126>
5. Bard AJ, Faulkner LR (2001) In *Electrochemical methods: fundamentals and applications*. Wiley 87–155
6. Jossen A (2006) *J Power Sources* 154:530–538
7. Chien YC, Liu H, Menon AS, Brant WR, Brandell D, Lacey MJ (2021) *ChemRxiv*. <https://chemrxiv.org/engage/chemrxiv/article-details/60cc4e4da5b6af1a487566d5>
8. Liu Y, Xu X, Sadd M, Kapitanova OO, Krivchenko VA, Ban J, Wang J, Jiao X, Song Z, Song J, Xiong S, Matic A, Liu Y, Ban J, Wang J, Jiao X, Song Z, Song J, Xu X, Sadd M, Xiong S, Matic A, Kapitanova OO, Krivchenko VA (2021) *Adv Sci* 8:2003301
9. Bauer HH (1968) *J Electroanal Chem Interfacial Electrochem* 16:419–432
10. Viswanathan V, Nørskov JK, Speidel A, Scheffler R, Gowda S, Luntz AC (2013) *J Phys Chem Lett* 4:556–560
11. Krauskopf T, Richter FH, Zeier WG, Janek J (2020) *Chem Rev* 120:7745–7794
12. Krauskopf T, Hartmann H, Zeier WG, Janek J (2019) *ACS Appl Mater Interfaces* 11:14463–14477
13. Krauskopf T, Mogwitz B, Rosenbach C, Zeier WG, Janek J (2019) *Adv Energy Mater* 9:1902568
14. Fauteux D (1985) *Solid State Ion* 17:133–138
15. Chen CH, Brosa Planella F, O'Regan K, Gastol D, Widanage WD, Kendrick E (2020) *J Electrochem Soc* 167:080534
16. Stolz L, Homann G, Winter M, Kasnatscheew J (2021) *Mater Today* 44:9–14
17. Stolz L, Homann G, Winter M, Kasnatscheew J (2021) *Data Brief* 34:106688, ISSN 2352-3409. <https://doi.org/10.1016/j.dib.2020.106688>
18. Stolz L, Röser S, Homann G, Winter M, Kasnatscheew J (2021) *J Phys Chem C* 125:18089–18097
19. Peled E, Menkin S (2017) *J Electrochem Soc* 164:A1703–A1719
20. Peled E (1979) *J Electrochem Soc* 126:2047–2051
21. Peled E, Golodnitsky D, Ardel G, Eshkenazy V (1995) *Electrochim Acta* 40:2197–2204
22. Stolz L, Winter M, Kasnatscheew J (2023) *J Electrochem Sci Eng* 13:715–724
23. Xu K (2014) *Chem Rev* 114:11503–11618
24. Zhang SS, Tran DT (2014) *J Mater Chem A Mater* 2:7383–7388
25. Zheng J, Gu M, Chen H, Meduri P, Engelhard MH, Zhang JG, Liu J, Xiao J (2013) *J Mater Chem A Mater* 1:8464–8470
26. Kasnatscheew J, Placke T, Streipert B, Rothermel S, Wagner R, Meister P, Laskovic IC, Winter M (2017) *J Electrochem Soc* 164:A2479–A2486
27. Schmuck R, Wagner R, Hörpel G, Placke T, Winter M (2018) *Nat Energy* 3:267–278
28. Placke T, Kloepsch R, Dühnen S, Winter M (2017) *J Solid State Electrochem* 21:1939–1964
29. Bieker G, Winter M, Bieker P (2015) *Phys Chem Chem Phys* 17:8670–8679
30. Zhang SS, Xu K, Jow TR (2004) *Electrochim Acta* 49:1057–1061
31. Stolz L, Hochstädt S, Röser S, Hansen MR, Winter M, Kasnatscheew J (2022) *ACS Appl Mater Interfaces* 14(9):11559–11566. <https://doi.org/10.1021/acsami.2c00084>
32. Mei BA, Munteshari O, Lau J, Dunn B, Pilon L (2018) *J Phys Chem C* 122:194–206
33. Mei BA, Lau J, Lin T, Tolbert SH, Dunn BS, Pilon L (2018) *J Phys Chem C* 122:24499–24511

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