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Review Article

Why nanoelectrochemistry is necessary in battery research?

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Abstract

The active materials constitute the heart of any battery so that unambiguous determination of their intrinsic properties is of essential importance to achieve progress in battery research. A variety of in situ techniques with high lateral resolution has been developed or adapted for battery research. Surprisingly, nanoelectrochemistry is not attracting sufficient attention from the battery community despite the existing examples of relevant in situ and highly resolved spatiotemporal information. Herein, the important role of nanoelectrochemistry in battery research is highlighted to help encourage its use in this field. In the first part, two examples in which the use of nanoelectrochemistry is a must are provided, that is, determination of intrinsic kinetics of active materials and understanding of relationships between particle structure and electrochemical activity. In the second part, pros and cons of three mature nanoelectrochemistry techniques in battery research, that is, particle-on-a-stick measurements, nanoimpact measurements, and scanning electrochemical probe microscopy, are discussed providing representative examples.

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Electrochemical energy storage, Battery, Active material, Nanoelectrochemistry, Single entity.

Introduction

Batteries have revolutionized our society, enabling commercial success of various smart devices used in day-to-day life, for example, portable electronics (mobile phones, tablets, and so on). More importantly, batteries are also the power sources of choice for the emerging electrified transport model as well as the energy storage technologies necessary for relying on renewable energy sources, for example, wind and solar radiation. Consequently, interest in developing new battery chemistries and improving existing battery technologies has gained much attention in recent years. Although the basic composition of a battery can be simply summarized into three elements, that is, positive electrode, electrolyte solution, and negative electrode, it is not a simple electrochemical device at all. Many electrochemical processes occur simultaneously, which hinder unambiguous investigation of the separate reactions and components. Aware of it, the battery research community has devoted much effort in developing and adapting advanced characterization techniques, which help putting together all pieces of the scientific puzzle. Without proper understanding of the individual elements of the complex system, progress in battery research at the cell level cannot be achieved. In general, efforts have been focused on the development of two groups of techniques. (1) *In situ* and *operando* techniques are of vital importance because information is obtained under relevant conditions (as close as possible to operating conditions) [1–3]. (2) Spatially resolved techniques allow the study of a group of individuals instead of evaluating the average response of thousands [4–6]. The battery research community has shown high interest in several advanced techniques, for example, in situ transmission electron microscopy as illustrated by the large number of citations attracted by pioneering works [7–9]. Surprisingly, efforts in nanoelectrochemistry and microelectrochemistry did not appear to have gained the expected attention by the battery research community, despite the fact that these techniques were shown to provide in situ information with spatiotemporal resolution in this field years ago [10–12]. At least two important aspects of nanoelectrochemistry are identified to contribute to it: why and how. On the one hand, the message of why nanoelectrochemistry is necessary in battery research may not have been convincingly transmitted. On the other hand, how nanoelectrochemical measurements are conducted and the differences among the various techniques may not have been sufficiently clear for nonspecialized scientists.

The overarching aim of this review article is to increase the scientific awareness of why nanoelectrochemistry is important for battery research. In the first part, the unique and relevant information that nanoelectrochemistry provides in battery research is highlighted. In the second part, the various nanoelectrochemical techniques used in battery research so far are revised.

Why is nanoelectrochemistry necessary in battery research?

Electrochemical processes occurring in a battery electrode

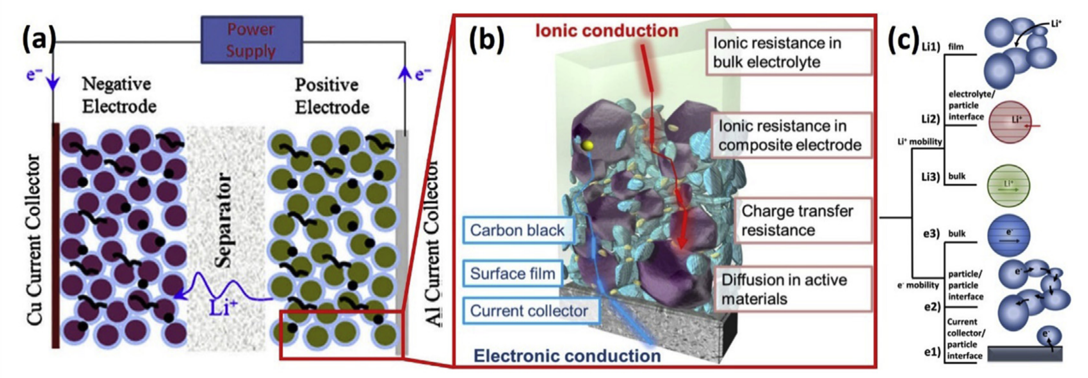
Although engineering of the battery cell is very important to improve the overall performance, the properties of the battery active materials, in which electrochemical reactions and energy storage take place, determine key parameters of the battery, for example, cell voltage, energy density, power density, safety, and cycle life. Therefore, more efforts are being devoted to study the intrinsic properties of active materials. However, a battery electrode is an ensemble of thousands of active material particles forming a porous film of tens of micrometers thick (Figure 1). Because energy storage mainly occurs in the bulk of the particles in battery materials (in contrast to capacitive or pseudocapacitive materials in which reactions only occur at the near surface), both electrons and ions must reach the electroactive center located in the bulk of an individual active material (Figure 1) [15]. Because many processes occur simultaneously in a battery electrode, approximations in which processes are neglected are necessary to simplify the evaluation and extract the intrinsic properties. Unfortunately, valid assumptions in other type of substrates/research fields are no longer valid for battery electrodes. Valid assumptions may even vary within the battery field depending on the nature of the active material. At this point, one can already sense that nanoelectrochemistry is of special interest for battery research. Two exemplary cases are selected and discussed in the following section to illustrate the potential and unique contribution of nanoelectrochemistry in battery research.

Intrinsic kinetics of active materials

Mass (ion) transport in the electrolyte often does not prevent the estimation of kinetic parameters by conventional electroanalytical techniques. However, this is not always the case as for the oxygen reduction reaction [16]. Nanoelectrochemistry has been successfully used in those cases in which mass transport plays a critical role [17—19]. For conventional battery electrodes, mass transport is known to limit battery performance when fast charging or low temperatures are required [20—22]. However, it is usually neglected when evaluating the properties of active materials. Electron transport to the electroactive center is usually not an issue in standard electrochemical measurements. However, electrons must cross many solid—solid interfaces to reach the active center in the case of battery electrodes [23]. Again, this parameter is usually disregarded in battery research.

Nanoelectrochemistry addresses simultaneously both issues for the determination of intrinsic kinetics of active materials. The evaluation of a single entity of battery material ensures enough mass transport from the electrolyte and enhances electron transport by reducing significantly the number of solid—solid interfaces Therefore, nanoelectrochemistry is a reliable and necessary analytical tool for the estimation of intrinsic properties, which are of key importance, for example, when new materials are proposed or storage mechanisms are elucidated.

Figure 1



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Involved steps during (de)lithiation. **(a)** Schematic of a lithium-ion battery being charged. Adapted with permission from Harris et al. [13]. **(b)** Schematic illustration of a composite electrode in lithium-ion batteries. Adapted with permission from Orikasa et al. [14]. **(c)** Schematic illustration of possible rate-limiting steps upon lithiation of an intercalation material. Adapted with permission from Löffler et al. [15].

Relationships between the active material structure and electrochemical activity

The electrochemical activity of active battery materials has been proposed to be influenced by the size [24–26] and morphology [26–28]. Tedious experiments were necessary, in which a group of particles with a range of sizes and morphologies are insulated and then evaluated. Even in this case, a range of sizes and morphologies are evaluated together with obtaining the average response of this narrower distribution. Obviously, the evaluation of a single entity is highly desired because it can unravel unexpected behaviors and correlations hindered under the average response of the heterogonous ensemble. The uniqueness of nanoelectrochemistry to elucidate structure–activity correlations has been widely demonstrated in other fields such as electrocatalysis [29–31].

How is nanoelectrochemistry applied in battery research?

Particle-on-a-stick measurements

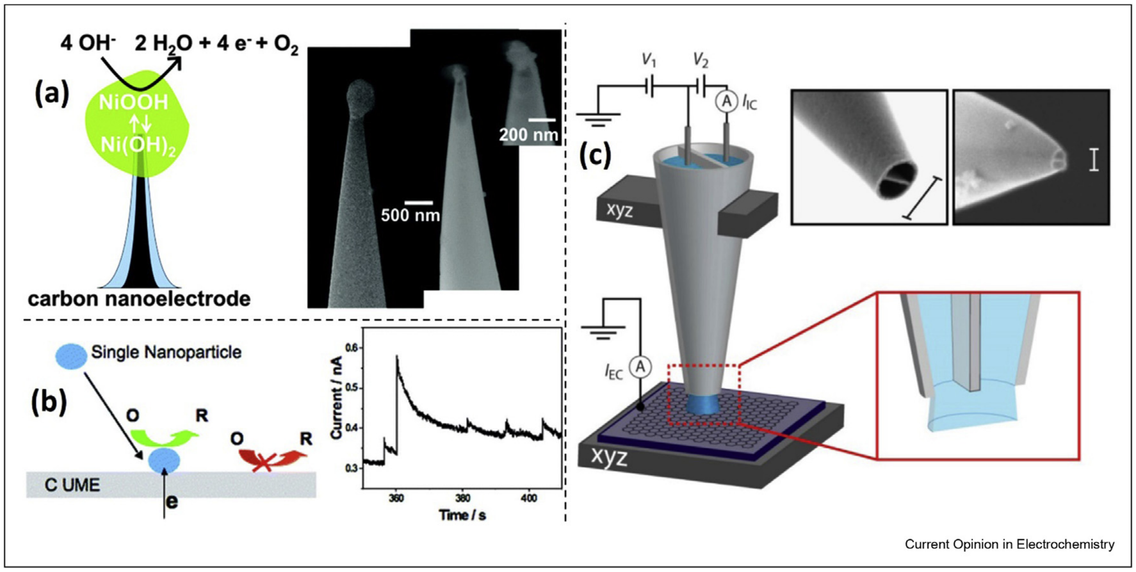
Fixation of a single particle in a nanoelectrode allows electrochemical evaluation of the individual particle (Figure 2a). The main advantages of this strategy are the following. (1) It does not require complicated instrumentation. (2) The generated electrochemical data are easily evaluated. (3) The particle can be evaluated using basically any type of electroanalytical method (chronoamperometry, cyclic voltammetry, and so on). (4) The particle is easily located for postanalysis, for example, SEM [32] and transmission electron microscopy [35,36]. Examples of particle-on-a-stick measurements can be found in other fields, for example, electrocatalysis [35–37], but also for battery materials, for example, $Ni(OH)_2$ [32], in which the influence of mass transport was discussed.

There are two major limitations. (1) Fixation of a presynthesized particle, for example, commercial material, is often not possible. (2) The sample preparation is time demanding because each particle needs to be fixed on one small electrode. Therefore, development of a fast and easily implementable universal approach to fix the particle on the electrode will certainly enhance interest in particle-on-a-stick measurements. The use of electrostatic forces appears to be a promising solution [38,39].

Nanoimpact measurements

Instead of fixing a single particle on a small electrode, the electrode is immersed in a suspension of particles. When the suspension is sufficiently diluted, the electrochemistry of a single entity can be evaluated during the short time of the collision with the electrode (Figure 2b) leading to the so-called nanoimpact measurements [40]. The main advantages of nanoimpact measurements are (1) simplicity of the experiment and (2) time-saving property because populations of a large distribution of characteristics are investigated in one single experiment. Nanoimpact measurements are been

Figure 2



Techniques of nanoelectrochemistry. **(a)** Illustration and SEM images of a particle stuck on a nanoelectrode. Adapted with permission from Clausmeyer et al. [32]. Royal Society of Chemistry. **(b)** Representation of a single particle collision on an ultramicroelectrode and the corresponding electrochemical response. Adapted with permission from Xiao and Bard [33]. Copyright 2016 American Chemical Society. **(c)** Schematic of the scanning electrochemical cell microscopy (SECCM) setup, with a transmission electron microscopy (TEM) image of a double-barreled quartz nanopipette (radius, r = 50 nm) inset. Adapted with permission from Unwin et al. [34]. Copyright 2016 American Chemical Society. SEM, scanning electron microscopy.

already used to investigate battery materials for aqueous media [41–45] and nonaqueous electrolytes (Li-ion battery electrolyte) [15].

The main limitations are as follows: (1) some electroanalytical methods are restricted owing to the short duration of the particle–electrode interaction and (2) the generated data are not simple to be analyzed by nonspecialists. The development of easy-to-use data analysis software for data analysis of nanoimpact measurements will certainly encourage the use of this powerful tool in a variety of fields including battery research.

Scanning electrochemical probe microscopy

A third option to study the electrochemical activity of single entities of battery materials is to use scanning electrochemical probe microscopy. The scanning electrochemical microscopy has been widely used to investigate battery electrodes, providing unique in situ and spatiotemporal resolved information [46]. However, the lateral resolution is still not sufficiently high to investigate single nanoparticles. The scanning electrochemical cell microscopy (SECCM) has emerged as a very suitable technique for the study of single entities [47]. The high lateral resolution of SECCM has been widely shown in other electrochemical processes [48–50]. There are several relevant examples of the successful application of SECCM for battery research [51–54]. Recently, SECCM was also installed inside an Ar-filled glove box to investigate the Li-ion battery electrode in nonaqueous electrolytes [55]. The main advantages are as follows: (1) the electrochemical activity of single particles can be evaluated by any conventional electroanalytical method, (2) the generated data are easy to be analyzed, and (3) the technique is fast and time-saving (many single particles can be evaluated in one single experiment).

The main limitation of SECCM for battery research is probably the perception of highly specialized instrumentation. Considering the potential of this technique, initial collaborations between battery and analytical chemistry communities are highly encouraged to break down this perception.

Conclusions and outlook

Conventional evaluation of macroelectrodes in battery research often prevents unambiguous determination of intrinsic properties of active materials. However, improvements in battery performances require reliable acquisition of intrinsic properties of active materials for a variety of purposes ranging from modelling, electrode design, material selection, battery management, and so on. For example, when a high value is reliably determined for the diffusion coefficient in the active material, mass transport through the battery electrode will be the diffusion-limiting step so that special attention must be paid to porosity/tortuosity of this porous electrode. Otherwise, denser and more compact electrodes could be pursued because diffusion inside the particle will anyways be the limiting aspect. Consequently, nanoelectrochemistry in battery research is necessary to deconvolute the various contributions to the average response obtained using conventional macroscopic ensembles of active materials. This step is of essential importance for understanding bottlenecks and storage mechanisms of the battery electrode, which in turn will lead us to better batteries.

There are at least three mature techniques available to conduct nanoelectrochemical measurements in battery research, that is, particle-on-a-stick measurements, nanoimpact measurements, and scanning electrochemical probe microscopy, each of them possessing intrinsic pros and cons. The various examples of unique information provided by these techniques will eventually bring the attention of the battery community. Still, there are two critical aspects for this to finally occur: (1) to find the right example that will mark a turning point and (2) to simplify the methods to facilitate its use by nonspecialists.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. Liu D, Shadike Z, Lin R, Qian K, Li H, Li K, Wang S, Yu Q, Liu M, Ganapathy S, Qin X, Yang Q, Wagemaker M, Kang F, Yang X, Li B: **Review of recent development of in situ/operando characterization techniques for lithium battery research**. *Adv Mater* 2019, **31**, 1806620, https://doi.org/10.1002/adma.201806620.

2. Boebinger MG, Lewis JA, Sandoval SE, McDowell MT: **Understanding transformations in battery materials using in situ and operando experiments: progress and outlook**. *ACS Energy Lett* 2020, **5**:335–345, https://doi.org/10.1021/acsenergylett.9b02514.

3. Tian J, Jiang T, Wang M, Hu Z, Zhu X, Zhang L, Qian T, Yan C: **In situ/operando spectroscopic characterizations guide the compositional and structural design of lithium–sulfur batteries**. *Small Methods* 2020, **4**:1900467, https://doi.org/10.1002/smtd.201900467.

4. Rodriguez JR, Aguirre SB, Pol VG: **Role of operando microscopy techniques on the advancement of sustainable**

sodium-ion battery anodes. *J Power Sources* 2019, **437**: 226851, https://doi.org/10.1016/j.jpowsour.2019.226851.

5. Kempaiah R, Vasudevamurthy G, Subramanian A: **Scanning probe microscopy based characterization of battery materials, interfaces, and processes**. *Nano Energy* 2019, **65**: 103925, https://doi.org/10.1016/j.nanoen.2019.103925.

6. Ren X, Zhang X, Xu R, Huang J, Zhang Q: **Analyzing energy materials by cryogenic electron microscopy**. *Adv Mater* 2020, **32**:1908293, https://doi.org/10.1002/adma.201908293.

7. Liu XH, Zheng H, Zhong L, Huang S, Karki K, Zhang LQ, Liu Y, Kushima A, Liang WT, Wang JW, Cho JH, Epstein E, Dayeh SA, Picraux ST, Zhu T, Li J, Sullivan JP, Cumings J, Wang C, Mao SX, Ye ZZ, Zhang S, Huang JY: **Anisotropic swelling and fracture of silicon nanowires during lithiation**. *Nano Lett* 2011, **11**:3312–3318, https://doi.org/10.1021/nl201684d.

8. Liu XH, Zhong L, Huang S, Mao SX, Zhu T, Huang JY: **Size-dependent fracture of silicon nanoparticles during lithiation**. *ACS Nano* 2012, **6**:1522–1531, https://doi.org/10.1021/nn204476h.

9. Liu N, Wu H, McDowell MT, Yao Y, Wang C, Cui Y: **A yolk-shell design for stabilized and scalable Li-ion battery alloy anodes**. *Nano Lett* 2012, **12**:3315–3321, https://doi.org/10.1021/nl3014814.

10. Lipson AL, Ginder RS, Hersam MC: **Nanoscale in situ characterization of Li-ion battery electrochemistry via scanning ion conductance microscopy**. *Adv Mater* 2011, **23**:5613–5617, https://doi.org/10.1002/adma.201103094.

11. Zampardi G, Ventosa E, La Mantia F, Schuhmann W: **In situ visualization of Li-ion intercalation and formation of the solid electrolyte interphase on TiO2 based paste electrodes using scanning electrochemical microscopy**. *Chem Commun* 2013, **49**:9347–9349, https://doi.org/10.1039/c3cc44576c.

12. Bülter H, Peters F, Schwenzel J, Wittstock G: **Spatiotemporal changes of the solid electrolyte interphase in lithium-ion batteries detected by scanning electrochemical microscopy**. *Angew Chem Int Ed* 2014, **53**:10531–10535, https://doi.org/10.1002/anie.201403935.

13. Harris SJ, Timmons A, Baker DR, Monroe C: **Direct in situ measurements of Li transport in Li-ion battery negative electrodes**. *Chem Phys Lett* 2010, **485**:265–274, https://doi.org/10.1016/j.cplett.2009.12.033.

14. Orikasa Y, Gogyo Y, Yamashige H, Katayama M, Chen K, Mori T, Yamamoto K, Masese T, Inada Y, Ohta T, Siroma Z, Kato S, Kinoshita H, Arai H, Ogumi Z, Uchimoto Y: **Ionic conduction in lithium ion battery composite electrode governs cross-sectional reaction distribution**. *Sci Rep* 2016, **6**:1–6, https://doi.org/10.1038/srep26382.

15. •• Löffler T, Clausmeyer J, Wilde P, Tschulik K, Schuhmann W, Ventosa E: **Single entity electrochemistry for the elucidation of lithiation kinetics of TiO_2 particles in non-aqueous batteries**. *Nano Energy* 2019, **57**:827–834, https://doi.org/10.1016/j.nanoen.2018.12.064.

This article opens up the possibility of conducting nano-impact measurements of single particles of commercial battery material in non-aqueous electrolyte inside an Ar-filled glovebox. The various limiting steps in the charging process of a battery electrode are discussed, clearly highlighting the need for nano-electrochemistry in battery research.

16. Dumitrescu I, Crooks RM: **Effect of mass transfer on the oxygen reduction reaction catalyzed by platinum dendrimer encapsulated nanoparticles**. *Proc Natl Acad Sci USA* 2012, **109**:11493–11497, https://doi.org/10.1073/pnas.1201370109.

17. Clausmeyer J, Schuhmann W: **Nanoelectrodes: applications in electrocatalysis, single-cell analysis and high-resolution electrochemical imaging**. *Trac Trends Anal Chem* 2016, **79**: 46–59, https://doi.org/10.1016/j.trac.2016.01.018.

18. German SR, Edwards MA, Ren H, White HS: **Critical nuclei size, rate, and activation energy of H2 gas nucleation**. *J Am Chem Soc* 2018, **140**:4047–4053, https://doi.org/10.1021/jacs.7b13457.

19. Gao R, Edwards MA, Qiu Y, Barman K, White HS: **Visualization of hydrogen evolution at individual platinum nanoparticles at a buried interface**. *J Am Chem Soc* 2020, **142**:8890–8896, https://doi.org/10.1021/jacs.0c02202.

20. Mao C, Ruther RE, Li J, Du Z, Belharouak I: **Identifying the limiting electrode in lithium ion batteries for extreme fast charging**. *Electrochem Commun* 2018, **97**:37–41, https://doi.org/10.1016/j.elecom.2018.10.007.

21. Yang XG, Zhang G, Ge S, Wang CY: **Fast charging of lithium-ion batteries at all temperatures**. *Proc Natl Acad Sci USA* 2018, **115**:7266–7271, https://doi.org/10.1073/pnas.1807115115.

22. • Yang XG, Liu T, Gao Y, Ge S, Leng Y, Wang D, Wang CY: **Asymmetric temperature modulation for extreme fast charging of lithium-ion batteries**. *Joule* 2019, **3**:3002–3019, https://doi.org/10.1016/j.joule.2019.09.021.

This paper clearly shows that ion transport through the battery electrode is the limiting step when charging fast. Asymmetric temperature for fast charging and slow discharging is shown to be a very effective strategy since higher temperature during charging enhances mass transport and thus improve the battery performances

23. Bai P, Bazant MZ: **Charge transfer kinetics at the solid-solid interface in porous electrodes**. *Nat Commun* 2014, **5**:1–7, https://doi.org/10.1038/ncomms4585.

24. Wagemaker M, Borghols WJH, Mulder FM: **Large impact of particle size on insertion reactions. A case for anatase Li_xTiO_2**. *J Am Chem Soc* 2007, **129**:4323–4327, https://doi.org/10.1021/ja067733p.

25. Madej E, La Mantia F, Schuhmann W, Ventosa E: **Impact of the specific surface area on the memory effect in Li-ion batteries: the case of anatase TiO_2**. *Adv Energy Mater* 2014, **4**:1400829, https://doi.org/10.1002/aenm.201400829.

26. Liu Z, Andreev YG, Robert Armstrong A, Brutti S, Ren Y, Bruce PG: **Nanostructured TiO_2(B): the effect of size and shape on anode properties for Li-ion batteries**. *Prog Nat Sci: Mater Int* 2013, **23**:235–244, https://doi.org/10.1016/j.pnsc.2013.05.001.

27. Wagemaker M, Mulder FM: **Properties and promises of nanosized insertion materials for li-ion batteries**. *Acc Chem Res* 2013, **46**:1206–1215, https://doi.org/10.1021/ar2001793.

28. Dylla AG, Xiao P, Henkelman G, Stevenson KJ: **Morphological dependence of lithium insertion in nanocrystalline TiO_2(B) nanoparticles and nanosheets**. *J Phys Chem Lett* 2012, **3**: 2015–2019, https://doi.org/10.1021/jz300766a.

29. Bentley CL, Kang M, Unwin PR: **Nanoscale surface structure-activity in electrochemistry and electrocatalysis**. *J Am Chem Soc* 2018, https://doi.org/10.1021/jacs.8b09828.

30. Tarnev T, Aiyappa HB, Botz A, Erichsen T, Ernst A, Andronescu C, Schuhmann W: **Scanning electrochemical cell microscopy investigation of single ZIF-derived nanocomposite particles as electrocatalysts for oxygen evolution in alkaline media**. *Angew Chem Int Ed* 2019, **58**:14265–14269, https://doi.org/10.1002/anie.201908021.

31. Choi M, Siepser NP, Jeong S, Wang Y, Jagdale G, Ye X, Baker LA: **Probing single-particle electrocatalytic activity at facet-controlled gold nanocrystals**. *Nano Lett* 2020, **20**: 1233–1239, https://doi.org/10.1021/acs.nanolett.9b04640.

32. Clausmeyer J, Masa J, Ventosa E, Öhl D, Schuhmann W: **Nanoelectrodes reveal the electrochemistry of single nickel-hydroxide nanoparticles**. *Chem Commun* 2016, **52**:2408–2411, https://doi.org/10.1039/c5cc08796a.

33. Xiao X, Bard AJ: **Observing single nanoparticle collisions at an ultramicroelectrode by electrocatalytic amplification**. *J Am Chem Soc* 2007, **129**:9610–9612, https://doi.org/10.1021/ja072344w.

34. Unwin PR, Güell AG, Zhang G: **Nanoscale electrochemistry of sp2 carbon materials: from graphite and graphene to carbon nanotubes**. *Acc Chem Res* 2016, **49**:2041–2048, https://doi.org/10.1021/acs.accounts.6b00301.

35. Yu Y, Gao Y, Hu K, Blanchard P-Y, Noël J-M, Nareshkumar T, Phani KL, Friedman G, Gogotsi Y, Mirkin MV: **Electrochemistry and electrocatalysis at single gold nanoparticles attached to carbon nanoelectrodes**. *ChemElectroChem* 2015, **2**:58–63, https://doi.org/10.1002/celc.201402312.

36. Aiyappa HB, Wilde P, Quast T, Masa J, Andronescu C, Chen Y, Muhler M, Fischer RA, Schuhmann W: **Oxygen evolution electrocatalysis of a single MOF-derived composite nanoparticle on the tip of a nanoelectrode**. *Angew Chem Int Ed* 2019, **58**: 8927–8931, https://doi.org/10.1002/anie.201903283.

37. Li Y, Cox JT, Zhang B: **Electrochemical responses and electrocatalysis at single Au nanoparticles**. *J Am Chem Soc* 2010, **132**:3047–3054, https://doi.org/10.1021/ja909408q.

38. Anderson TJ, Zhang B: **Single-Nanoparticle electrochemistry through immobilization and collision**. *Acc Chem Res* 2016, **49**: 2625–2631, https://doi.org/10.1021/acs.accounts.6b00334.

39. Wilde P, Barwe S, Andronescu C, Schuhmann W, Ventosa E:
• **High resolution, binder-free investigation of the intrinsic activity of immobilized NiFe LDH nanoparticles on etched carbon nanoelectrodes**. *Nano Res* 2018, **11**:6034–6044, https://doi.org/10.1007/s12274-018-2119-4.

This work shows a very simple strategy to fix particles on nanoelectrodes, which is based on electrostatic forces. The lack of binder allows better evaluation of lifespan of the active materials.

40. Patrice FT, Qiu K, Ying Y-L, Long Y-T: **Single nanoparticle electrochemistry**. *Annu Rev Anal Chem* 2019, **12**:347–370, https://doi.org/10.1146/annurev-anchem-061318-114902.

41. Zampardi G, Batchelor-McAuley C, Kätelhön E, Compton RG:
•• **Lithium-ion-Transfer kinetics of single $LiMn_2O_4$ particles**. *Angew Chem* 2017, **129**:656–659, https://doi.org/10.1002/ange.201610485.

This work demonstrates for the first time that battery materials can be studied using nano-impact measurements reporting intrinsic kinetics parameters of LiMn2O4.

42. Zampardi G, Sokolov SV, Batchelor-McAuley C, Compton RG: **Potassium (De-)insertion processes in prussian blue particles: ensemble versus single nanoparticle behaviour**. *Chem Eur J* 2017, **23**:14338–14344, https://doi.org/10.1002/chem.201703175.

43. Rano S, Laberty-Robert C, Ngo K, Sánchez-Sánchez CM, Vivier V: **Characterization of $LiCoO_2$ nanoparticle suspensions by single collision events**. *Phys Chem Chem Phys* 2019, **21**:5416–5423, https://doi.org/10.1039/c9cp00199a.

44. Xu W, Zhou Y, Ji X: **Lithium-ion-Transfer kinetics of single LiFePO4 particles**. *J Phys Chem Lett* 2018, **9**:4976–4980, https://doi.org/10.1021/acs.jpclett.8b02315.

45. Xu W, Tian Y, Zou G, Hou H, Ji X: **Single particles electrochemistry for batteries**. *J Electroanal Chem* 2020:113935, https://doi.org/10.1016/j.jelechem.2020.113935.

46. Ventosa E, Schuhmann W: **Scanning electrochemical microscopy of Li-ion batteries**. *Phys Chem Chem Phys* 2015, **17**: 28441–28450, https://doi.org/10.1039/c5cp02268a.

47. Wahab OJ, Kang M, Unwin PR: **Scanning electrochemical cell microscopy: a natural technique for single entity electrochemistry**. *Curr Opin Electrochem* 2020, **22**:120–128, https://doi.org/10.1016/j.coelec.2020.04.018.

48. Mariano RG, McKelvey K, White HS, Kanan MW: **Selective increase in CO_2 electroreduction activity at grain-boundary surface terminations**. *Science* 2017, **358**:1187–1192, https://doi.org/10.1126/science.aao3691.

49. Daviddi E, Chen Z, Beam Massani B, Lee J, Bentley CL, Unwin PR, Ratcliff EL: **Nanoscale visualization and multiscale electrochemical analysis of conductive polymer electrodes**. *ACS Nano* 2019, https://doi.org/10.1021/acsnano.9b06302.

50. Ornelas IM, Unwin PR, Bentley CL: **High-throughput correlative electrochemistry-microscopy at a transmission electron microscopy grid electrode**. *Anal Chem* 2019, **91**:14854–14859, https://doi.org/10.1021/acs.analchem.9b04028.

51. Takahashi Y, Kumatani A, Munakata H, Inomata H, Ito K, Ino K, Shiku H, Unwin PR, Korchev YE, Kanamura K, Matsue T: **Nanoscale visualization of redox activity at lithium-ion battery cathodes**. *Nat Commun* 2014, **5**:1–7, https://doi.org/10.1038/ncomms6450.

52. Kumatani A, Takahashi Y, Miura C, Ida H, Inomata H, Shiku H, Munakata H, Kanamura K, Matsue T: **Scanning electrochemical cell microscopy for visualization and local electrochemical activities of lithium-ion (de) intercalation process in lithium-ion batteries electrodes**. *Surf Interface Anal* 2019, **51**:27–30, https://doi.org/10.1002/sia.6538.

53. Tao B, Yule LC, Daviddi E, Bentley CL, Unwin PR: **Correlative**
•• **electrochemical microscopy of Li-ion (De)intercalation at a series of individual $LiMn_2O_4$ particles**. *Angew Chem Int Ed* 2019, **58**:4606–4611, https://doi.org/10.1002/anie.201814505.

In this work, the high resolution of SECCM to investigate single entities of battery materials is demonstrated, encouraging the use of this technique in battery research.

54. Inomata H, Takahashi Y, Takamatsu D, Kumatani A, Ida H, Shiku H, Matsue T: **Visualization of inhomogeneous current distribution on ZrO_2-coated $LiCoO_2$ thin-film electrodes using scanning electrochemical cell microscopy**. *Chem Commun* 2019, **55**:545–548, https://doi.org/10.1039/c8cc08916g.

55. Takahashi Y, Yamashita T, Takamatsu D, Kumatani A,
• Fukuma T: **Nanoscale kinetic imaging of lithium ion secondary battery materials using scanning electrochemical cell microscopy**. *Chem Commun* 2020, https://doi.org/10.1039/D0CC02865G.

This article represents a pioneering work in the use of SECCM inside a glovebox for the investigation of battery materials in non-aqueous electrolytes.