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Improved *Operando* Raman Cell Configuration for Commercially-Sourced Electrodes in Alkali-Ion Batteries

Timothy E. Rosser,^{1,*} Edmund J. F. Dickinson,^{1,*} Rinaldo Raccichini,¹ Katherine Hunter,² Andrew D. Searle,² Christopher M. Kavanagh,² Peter J. Curran,² Gareth Hinds,^{1,*} Juyeon Park,^{1,*} and Andrew J. Wain^{1,*}

¹National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, United Kingdom

²Deregallera Ltd., Unit 2 De Clare Court, Pontywindy Industrial Estate, Caerphilly CF83 3HU, United Kingdom

Operando Raman spectroscopy is a well-established technique for monitoring chemical changes in active materials during electrochemical cycling of alkali-ion cells. To date, however, its application to the study of commercial electrodes under realistic operating conditions has been severely limited by cell design constraints. We present here an improved configuration for performing *operando* Raman spectroscopy on coated metal foil electrodes used in standard laboratory cell testing. Electrochemical modeling predicts much improved lithiation homogeneity compared to a previously used configuration; this observation is validated experimentally for a commercially-sourced graphite electrode. The new configuration delivers improved electrochemical performance at higher specific currents than was previously possible, ensuring that Raman measurements at a single location are representative of the entire electrode. Finally, the broad applicability of the configuration is demonstrated through a study of hard carbon sodium-ion negative electrodes over 50 cycles. These results provide a new configuration for performing reliable, validated *operando* Raman spectroscopy on commercial battery electrodes, as well as establishing a general methodological framework for the validation of *operando* spectroscopic techniques to ensure that their performance is relevant to the practical systems to which they are applied.

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The widespread use of electrochemical energy storage in sectors such as transport is essential if targets are to be met for large-scale decarbonization and, by extension, reduced CO₂ emissions. This goal requires the continued development of devices with higher capacities and longer lifetimes, with alkali-ion technology likely to play a major role. Key to this progress is the use of improved *operando* techniques for monitoring material properties during few-cycle mechanistic studies and many-cycle stability/degradation studies.² Degradation processes especially will be very sensitive to operating parameters, and as such if a technique is to be truly *operando*, the extent to which the nature of the *operando* measurement constrains cycling and materials properties must be understood and mitigated as much as possible.

Raman spectroscopy is one such technique used to characterize the chemical properties of active materials in alkali-ion battery electrodes, by measuring the frequencies of chemical bond vibrations.³ Since these chemical properties, and by consequence vibrational modes, change as a result of ion insertion/extraction and other mechanisms of charge storage in such devices, *operando* Raman spectroscopy is of great importance for both mechanistic characterization of novel electrode materials^{4–6} and longer-term degradation studies.⁷ However, performing these measurements places certain constraints on cell design. In particular, this technique requires an optical pathway (typically in the visible or near-infrared) for incident and Raman-scattered light to pass between the spectrometer and the electrode of interest, which is not possible in conventional alkali-ion cells due to opacity of cell components. Deviations are thus necessary from an “ideal” cell configuration (where electrolyte transport is not limiting), which have an unknown, typically poorly understood, and potentially profound impact on the cell chemistry. Conclusions from *operando* Raman measurements therefore cannot be used to infer electrode performance under “real world” operating conditions without rigorous validation of the influence of cell configuration.

Several cell configurations for performing Raman spectroscopy on cycled electrodes (herein referred to as “Raman cells”) exist. Many Raman cell designs use either electrodes manufactured by depositing an active material slurry directly onto a mesh current collector⁸ or a separator,⁹ or free-standing electrodes pressed against holed current collectors.^{5,10–13} These offer the advantage of a “face-to-face” (plane parallel) alignment of electrodes, and consequently ion transport close to that of an optimal cell, as well as visible light access through holes in the current collector to the back of the electrode for Raman spectroscopy measurements. Such cells require the preparation of bespoke electrodes dedicated to these experiments, which is suitable for exploratory studies on novel materials. However, the application of the technique to commercial electrodes is more challenging as the cell configuration is unlikely to be sufficiently representative of cell testing with standard coated metal foil electrodes. For instance, properties such as residual water content in the electrodes and delamination of active material, which have a direct influence on cell performance and lifetime,^{14,15} will depend on specific fabrication and processing parameters and will not necessarily be replicated in a bespoke electrode for Raman spectroscopy measurements. Therefore, capability for performing reliable *operando* Raman spectroscopy on conventionally manufactured (coated foil) electrodes, rather than bespoke electrodes, is essential to ensure performance that is more representative of that in standard laboratory cell testing.

Only a handful of *operando* Raman studies have used coated foil electrodes, as opposed to bespoke electrodes.^{16–20} One such configuration allows light to pass through a transparent cell window and then holes in both the Li or Na counter electrode and separator, all positioned between the working electrode and the objective lens.^{18–20} Given that the working electrode is facing the counter electrode, electrochemical performance is unlikely to be severely disrupted. However, this configuration requires the incident laser and scattered light to penetrate a relatively thick layer of electrolyte solution (typically >100 μm, the combined thickness of the separator and counter electrode), which can lead to the Raman spectra being dominated by electrolyte and solvent peaks¹⁷ and, particularly in the case of hexafluorophosphate electrolytes, fluorescence. The latter issue

*Electrochemical Society Member.

^zE-mail: andy.wain@npl.co.uk

has previously been overcome using perchlorate electrolytes,²¹ but the overwhelming preference in commercial cells is for hexafluorophosphate electrolytes, and so a suitable Raman cell must accommodate these.

An alternative configuration for coated foil electrodes utilizes a strip (1–2 mm width) of electrode pressed with the active material against a transparent window and with the current collector facing the counter electrode.²² This configuration has been proposed by manufacturers of a commercially available optical test cell with current collector-backed electrodes,²³ and is depicted in Fig. 1a, referred to herein as the “Standard configuration.” Whilst *operando* Raman spectra can be obtained from the cycling cell at low current densities,²⁴ local inhomogeneity of lithiation across the electrode due to slow electrolyte diffusion is acknowledged.²² Indeed, in our experience of cycling a graphite lithium-ion battery (LIB) electrode in this configuration, it is apparent from visual inspection that the distribution of lithiation across the electrode at a given State of Charge (SOC) is highly inhomogeneous (Fig. S1 (available online at stacks.iop.org/JES/168/070541/mmedia)); gold coloration, indicative of extensive lithiation, is observed towards the outer edges of the electrode whilst the central region remains apparently uncharged. Therefore, any spectra obtained would be a function of measurement location as well as cell voltage in a manner that is specific to the cell geometry used and not necessarily relevant to the electrode when used under practical operating conditions.

To remedy this, the electrode must be made more uniformly accessible to electrolyte, while still leaving sufficient access to the Raman laser light. The solution developed here is to place a glass fiber separator with a small central hole as a spacer between the working electrode strip and the transparent sapphire window, which we refer to hereafter as the “Spacer configuration” (Fig. 1b). Upon saturation of the separator with electrolyte, this allows contact with electrolyte solution on all macroscopic faces of the electrode, alleviating the transport limitation and thus affording electrochemical conditions with closer relevance to practically used systems. This proposed cell configuration also offers the advantage of using only commercially available parts and thus does not require specialist cell or electrode manufacture capability.

The aim of this study is to develop a framework for the rigorous evaluation of our modified cell configuration for *operando* Raman spectroscopy of electrochemical energy storage electrodes, and its

comparison with the existing Standard configuration. Our methodology begins with theoretical prediction of the electrochemical performance and spatial inhomogeneity of lithiation for different possible cell configurations, followed by experimental validation of these electrochemical properties, and verification that the Raman spectra obtained match literature examples acquired in configurations optimized for spectral quality. Finally, the broad applicability of the modified configuration is demonstrated in the study of a hard carbon Na-ion negative electrode over 50 sodiation/desodiation cycles. These studies are intended to give confidence in the applicability of *operando* Raman measurement results to observations from tests in cells manufactured using coated metal foil electrodes, by establishing a Raman cell configuration for which the electrochemical performance does not deviate significantly from that of a lab-scale test cell.

Methods Section

Theory and modeling.—The two Raman cell configurations (summarized in Fig. 1) were assessed by electrochemical modeling of the designs. For brevity, only key details of the model implementation are summarized here; the model equations and input parameters, including their sources, are documented comprehensively in the Supporting Information.

The simulations were conducted using a standard Newman-type electrochemical model.^{25–27} This model describes a non-ideal binary electrolyte in which current density, lithium electrolyte flux and insertion reaction rate within the cell are computed self-consistently with the temporally and spatially varying electric field, lithium electrolyte concentration, and degree of lithiation in the particles of active insertion material.²⁸ The model was implemented in a plane 2D schematic geometry oriented in the macroscopic cross-section of the electrode strip and separators (normal to the long axis of the strip) with the geometry either including (Spacer configuration) or excluding (Standard configuration) the additional separator region. Diffusion in particles of insertion material was described in an additional spherical 1D coordinate to create a 2D + 1D model. Standard material and electrochemical properties were assumed for the Li and graphite electrodes, for the transport properties of 1 M LiPF₆ electrolyte in 1:1 w/w ethylene carbonate/diethyl carbonate (EC/DEC) solvent, and for the morphological properties (porosity and tortuosity) of the glass fiber separators and graphite electrode. All numerical

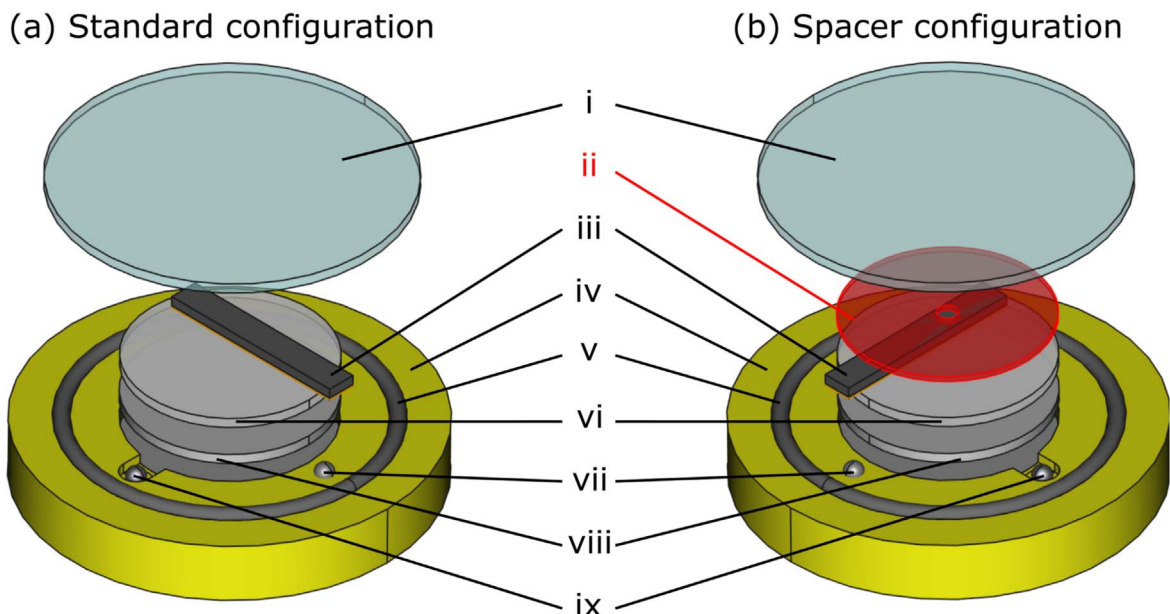


Figure 1. Schematic of the cell designs described in this paper - Standard configuration (a) and Spacer configuration (b). (i) Sapphire window, (ii) holed spacing separator (red color for illustration only), (iii) coated metal foil working electrode (active material facing up) (iv) PEEK cell base, (v) O ring, (vi) glass fiber separator, (vii) working electrode contact, (viii) Li(Na) counter electrode and (ix) Li(Na) reference electrode.

computation was performed in COMSOL Multiphysics 5.5 [COMSOL AB, www.comsol.com] on standard desktop computing hardware.

As output, the model predicted galvanostatic charge-discharge transients for each configuration, from which electrode utilization could be assessed as a function of specific current ($i_{sp}/\text{mA g}^{-1}$). Additionally, differential capacity-voltage plots (dQ/dE plots) were extracted by numerical differentiation of the voltage-time response. The predicted spatial profile of lithiation in the working electrode was also studied as a metric for inhomogeneity of electrode utilization and hence an indication of the degree to which a Raman spectrum measured at any given location (on the imaging plane at the top of the working electrode) is representative of the overall SOC of the electrode.

Materials.—For Li-ion Raman cell measurements, the working electrode was a commercial graphite sheet on Cu. The active material (graphite) loading was measured as 6.6 mg cm^{-2} , and the total electrode thickness (measured with a Mitutoyo ABSOLUTE Digimatic thickness gauge) was approximately $71 \pm 1.3 \mu\text{m}$ ($12 \pm 0.5 \mu\text{m}$ Cu foil and $59 \pm 1.3 \mu\text{m}$ active material and binders; error based on standard deviation of four electrode samples). The electrolyte solution was 1.0 M LiPF_6 in ethylene carbonate/diethyl carbonate (EC/DEC) in a 1:1 volumetric ratio (anhydrous battery grade, Sigma-Aldrich) and was used as received. Counter electrodes were 9 mm diameter disks cut from a 19 mm width Li ribbon (Sigma-Aldrich; 99.9% trace metals basis; 0.075 mm thickness).

For Na-ion cell measurements (Raman cell and “lab-scale” non-Raman cell), the working electrode was hard carbon/sodium alginate (9:1) deposited on Al foil ($18 \mu\text{m}$). The hard carbon (code B187) provided by Deregallera Ltd. is a low furnace temperature, low cost, high surface area, low capacity material, produced by a proprietary synthesis process utilizing a sustainable biowaste stream. The absence of a low potential plateau, characteristic of conventional hard carbons, is of particular interest in the context of the very high power applications for which this material is tailored. The improved cell configuration presented in this work is therefore a key enabling technology for continued development of solid-electrolyte interphase (SEI) formation protocols of immediate commercial relevance to Deregallera. The electrolyte solution was 1.0 mol kg^{-1} sodium trifluoromethanesulfonimide (NaTFSI , Alfa Aesar, purity $>97\%$), dissolved in propylene carbonate (PC, Sigma-Aldrich, Anhydrous $\text{H}_2\text{O} < 50 \text{ ppm}$, 99.7% purity). The reference and counter electrodes were Na metal (Alfa Aesar, 99.95% trace metals basis), with the counter electrode approximately 0.5 mm thick.

For Raman cell measurements, electrodes were cut into strips of approximately 16 mm by 1.5 mm, and working and counter electrodes were separated by a glass fiber separator (Whatman, 1 mm uncompressed thickness). In the Spacer configuration, the working electrode and window were separated by a Whatman GF/A glass fiber separator (0.26 mm uncompressed thickness) with a 1.6 mm diameter central hole.

Cell construction.—Cell construction was performed in an Ar-filled glovebox (MBRAUN, LABmaster Pro), with oxygen and water levels maintained below 1 ppm. All components were dried in a tubular glass vacuum oven (Buchi, pressure $< 1 \text{ mbar}$) at a minimum temperature of 80°C overnight. An EL-CELL ECC-Opto-Std spectroelectrochemical cell was used for all Raman cell measurements. The cells were assembled according to the schematic diagrams shown in Fig. 1. The Li/Na counter electrode was placed on top of a stainless steel plunger, topped with a glass fiber separator and then the working electrode strip (current collector side facing the counter electrode). For the Spacer configuration only, a second, 0.25 mm glass fiber separator (compressed to a thickness of approximately $70 \mu\text{m}$, measured in situ using optical microscopy) was placed on top of the working electrode strip, with a 1.6 mm diameter central hole exposing part of the working electrode to laser light from above. The reference electrode²⁹ was a small circular piece (approximately 1 mm diameter) of Li/Na. The cells were

sealed with a sapphire window and an EPDM O-ring (selected for electrolyte resistance), held in place by a metallic cell top. Finally, electrolyte solution was introduced by connecting a syringe containing approximately 0.5 ml electrolyte solution (see “Materials” section for electrolyte composition) to the filling port of the sealed cell via a polyetheretherketone (PEEK) tube and airtight connector. The cell was evacuated by pulling the syringe plunger, which was then released to fill the cell with approximately $100 \mu\text{l}$ solution.

For lab scale cell measurements (Fig. S5 only), an EL-Cell PAT-Cell was used with 18 mm diameter hard carbon working and sodium counter electrodes, a sodium ring reference electrode and glass fiber (Whatman GF/A) separator. The volume of electrolyte solution (as specified in “Materials” section) was 0.15 ml.

Electrochemical cycling.—Galvanostatic electrochemical cycling was performed using an Autolab PGSTAT302N potentiostat/galvanostat (for Raman cell measurements) and Biologic VMP-300 galvanostat, using the specified value of i_{sp} . Potentials were recorded relative to a Li^+/Li or Na^+/Na reference electrode as appropriate and lower cut-off voltages of 0.005 V vs Li^+/Li ³⁰ and 0.02 V vs Na^+/Na (to avoid any Na plating³¹) were used for galvanostatic cycling for Li-ion and Na-ion cell measurements, respectively. Cells were allowed to equilibrate for at least 3 hours after assembly, until the open circuit potential reached a stable value, and then subjected to an initial cycle at $i_{sp} = 10 \text{ mA g}^{-1}$ before collecting the data presented herein. Electrochemical cycling was performed at 20°C with laboratory temperature control of $\pm 0.5^\circ\text{C}$.

Raman spectroscopy.—Raman spectroscopy measurements were performed on a Horiba LabRAM HR Evolution spectrometer. For Li-ion cell measurements, a 532 nm laser was used with the power attenuated to below 1 mW, while for Na-ion cell measurements a 785 nm laser was used with power attenuated to approximately 35 mW (the higher wavelength was preferred in the latter case to minimize fluorescence, which was more problematic for the Na electrolyte). A “DuoScan” beam rastering feature was used to minimize the laser power at individual locations, with the diameter of the effective beam spot increased to $10 \mu\text{m}$. Sample locations were assessed optically following spectra and by repeat spectra for damage caused by localized heating; none was observed using these parameters. The spectrometer was configured with a 600 lines/mm grating, $100 \mu\text{m}$ hole and $150 \mu\text{m}$ slit apertures, and a $50 \times$ super-long working distance objective lens. Measurements typically consisted of $10 \times 30 \text{ s}$ acquisitions (unless otherwise stated), and for *operando* experiments were recorded once per hour during continuous galvanostatic cycling.

Results

Assessment of cell configurations using electrochemical modeling.—To predict and understand the effect of cell geometry on the SOC distribution and overall realizable capacity of working electrodes in cell configurations suitable for *operando* Raman spectroscopy, the electrochemical performance and spatial charge distribution of the Standard and Spacer configurations were predicted by mathematical modeling. Graphite was chosen as a model active material for this study due to its importance in commercial applications and its distinct and well-characterized lithiation-dependent Raman spectrum.^{10,12,17}

For a graphite electrode in the Standard configuration, charging was simulated from the high voltage cut-off (assuming formation has already taken place) at a low i_{sp} of 10 mA g^{-1} , to 40% of total SOC (for the whole electrode). The resulting predicted spatial distribution of degree of lithiation is shown in Fig. 2a. Predicted local degree of lithiation varies from < 0.25 in the region more than $350 \mu\text{m}$ from the edge of the electrode strip to a degree of lithiation of approximately 1 (LiC_6) within $100 \mu\text{m}$ of the electrode edge. Given the approximate micrometer sampling area of a Raman measurement, it would therefore be impossible, except by chance, to obtain a spectrum that

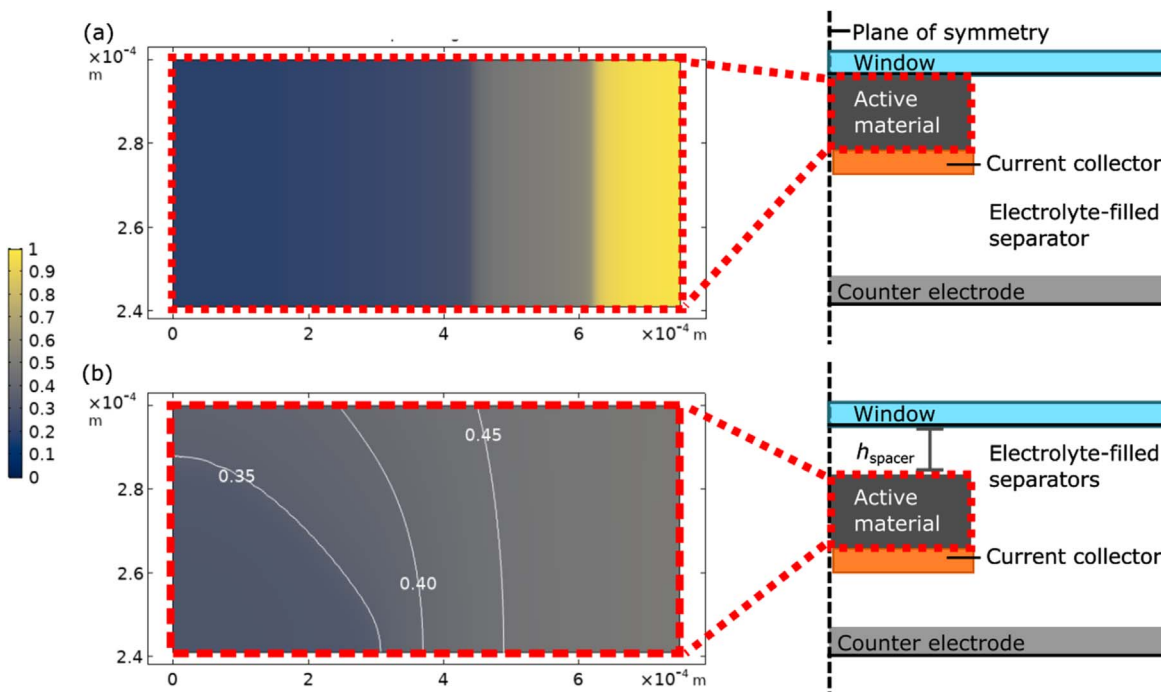


Figure 2. Schematics of simulated geometries for (a) Standard configuration ($h_{\text{spacer}} = 0 \mu\text{m}$) and (b) Spacer configuration ($h_{\text{spacer}} = 70 \mu\text{m}$), with simulated color profiles of local degree of lithiation in working electrode cross-sections, following charging at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$ to 40% SOC (averaged across the entire electrode). $0 \mu\text{m}$ on the x -axis represents the center of the electrode strip and $7.7 \mu\text{m}$ represents the edge of the electrode strip. Color legend: degree of lithiation.

accurately represents the overall SOC of the electrode. This electrochemical inhomogeneity is attributed to the non-uniform accessibility of the working electrode to electrolyte, as the impermeable window limits ingress of Li^+ in the vertical (electrode-normal) direction. Therefore, Li^+ reaching the center of the electrode must travel laterally via electrolyte migration (or diffusion) through the porous electrode over a distance of hundreds of μm . This process will be very slow compared to transport only through the thickness of the porous electrode (tens of μm),²² and hence the electrochemical performance in this configuration deviates significantly from a conventional cell. Whilst some inhomogeneity in lithiation would be expected in electrodes cycled in any cell,³² these predicted results correlate the inhomogeneity observed here to the specific cell geometry (Standard configuration) and predict that results obtained from Raman measurements at specific points on the electrode in Standard configuration cannot be interpreted as general for the electrode.

The corresponding predicted spatial distribution of degree of lithiation for a graphite electrode in the Spacer configuration after charging at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$ to 40% overall SOC is shown in Fig. 2b. The range of degree of lithiation is much narrower than in the Standard configuration, with values ranging from 0.37 to 0.48 across the top surface of the active material, facing the window. This represents a significant improvement in homogeneity brought about by the introduction of the spacing separator, which greatly increases the contact area of the active material with electrolyte in the separator, and permits Li^+ ingress from above. Corresponding plots of the spatial distribution of degree of lithiation in the Spacer configuration are shown for higher specific currents in Fig. S2 (noting that for $i_{\text{sp}} > 10 \text{ mA g}^{-1}$, 40% overall SOC is not attainable within the defined voltage window in the Standard configuration), exhibiting increased inhomogeneity with increasing specific current.

A direct manifestation of this predicted difference in lithiation homogeneity is also observed electrochemically in the predicted differential capacity (dQ/dE) plots shown in Fig. 3. Peaks in these plots show the potentials at which electrochemical processes occur during galvanostatic cycling. For graphite, peaks are expected at $E = 0.205 \text{ V}$, 0.115 V and 0.078 V vs Li^+/Li , accounting for transitions

to increasingly lithiated phases.³³ In the predicted cathodic scan at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$ for the Standard configuration (Fig. 3a), these peaks are poorly resolved, with resolution further deteriorating at higher i_{sp} . The poor resolution of the peaks in the differential capacity analysis can be explained by the inhomogeneous lithiation of the electrode causing the characteristic electrochemical phase transitions to be dispersed across a range of cell voltages, depending on the exact location in the electrode.

Conversely, in a model of the Spacer configuration with an especially thick separator of $250 \mu\text{m}$ between the electrode face and the window (Fig. 3c), the predicted differential capacity peaks at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$ and 25 mA g^{-1} are much better resolved, indicating that each successive electrochemical stage during charging occurs near-uniformly across the whole electrode, within a narrow potential range. For instance, in Fig. 2b, the range of degree of lithiation is entirely confined to that corresponding to the phase change $\text{Li}_{0.5}\text{C}_6 \rightarrow \text{LiC}_6$, i.e. the whole electrode is confined to one “peak” of the dQ/dE plot at this instance. Much less variance is predicted in the spatial distribution of localized degree of lithiation compared to the average value, and therefore any Raman spectra recorded are likely to be representative of the whole electrode at a given SOC; performance is nonetheless still predicted to deteriorate at the highest specific currents studied (see also Fig. S2). The true distance between the working electrode and the window in our experimental measurements is $70 \mu\text{m}$, and the predicted differential capacity plot (Fig. 3b) for this geometry also shows improved dQ/dE peak resolution compared to the Standard configuration, but not to the same extent as with the larger separation in Fig. 3c. Overall, however, the simulations present a consistent observation of increased homogeneity with increased spacing separator thickness, and decreased specific current.

Electrochemical characterisation of cell configurations.—

Given that the aim of performing *operando* characterization measurements such as Raman spectroscopy on a cycling electrode is to gain additional chemical insight into electrochemical observations obtained using typical laboratory-scale cells in material screening

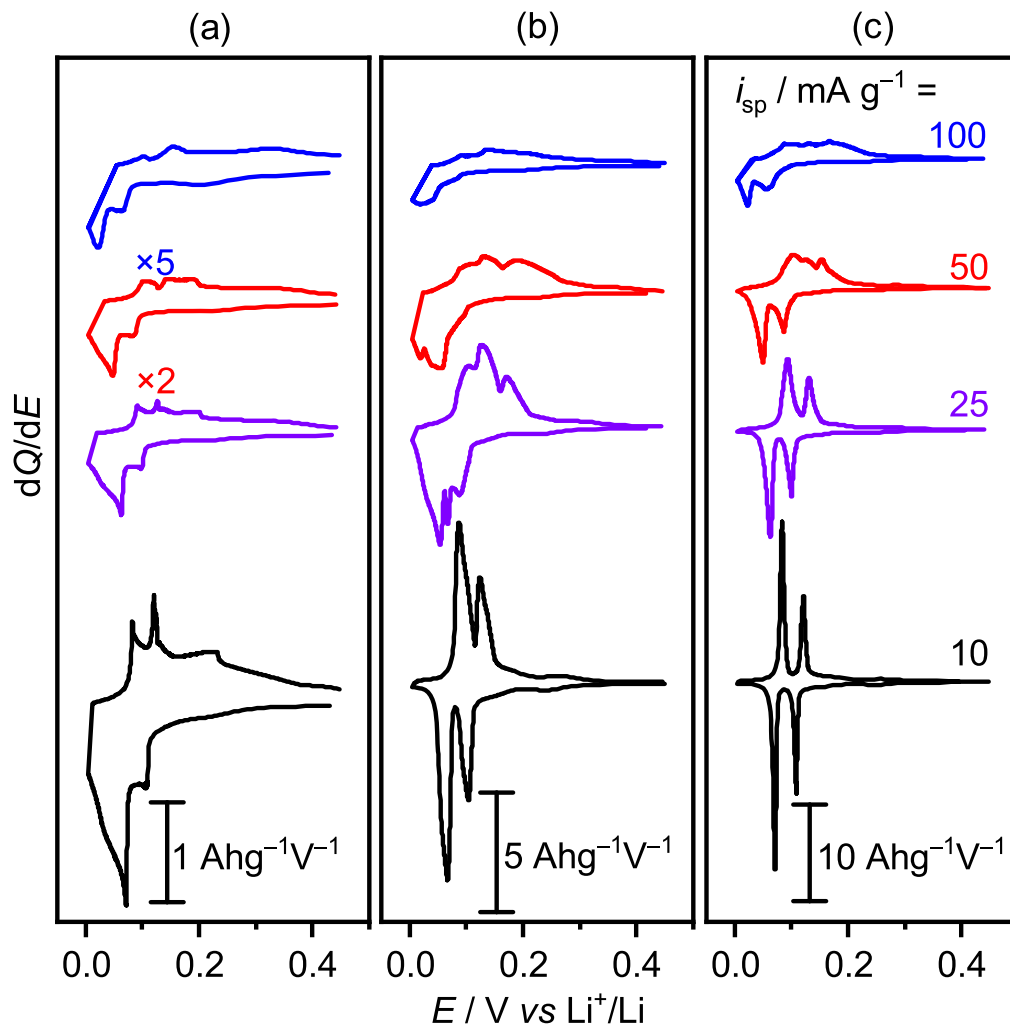


Figure 3. Predicted differential capacity-voltage (dQ/dE) plots of a modelled graphite working electrode in a Standard configuration cell (a), and in Spacer configuration cells with (b) 70 μm and (c) 250 μm compressed thickness spacing separators at specific currents of 10 (black line), 25 (purple), 50 (red) and 100 (blue) mA g^{-1} .

and electrode optimization, it is essential that the electrochemical conditions and performance of the complementary techniques are matched as closely as possible. Therefore, specific capacities obtained across a range of i_{sp} for each Raman cell configuration were obtained experimentally and compared to the theoretical capacities. Graphite electrodes were assembled into the three-electrode cell configurations described in Fig. 1 and were subjected to electrochemical cycling at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$, 25 mA g^{-1} , 50 mA g^{-1} and 100 mA g^{-1} , with the average lithiation and delithiation capacities from three separate cells summarized in Figs. 4a and 4b, and representative lithiation/delithiation profiles shown in Fig. S3. For the Standard configuration, the specific capacity at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$ is about 300 mA h g^{-1} , but the average values at higher specific currents are much lower, down to $53 \pm 9 \text{ mA h g}^{-1}$ at 50 mA g^{-1} and $27 \pm 4 \text{ mA h g}^{-1}$ at $i_{\text{sp}} = 100 \text{ mA g}^{-1}$. The latter values are as much as an order of magnitude lower than the theoretical capacity of 372 mA h g^{-1} expected for a graphite negative electrode, and therefore the extent of the utilization of active material, and thus the electrode chemistry, will be dramatically different from that in a standard laboratory test cell.

Conversely, in the Spacer configuration, the specific capacity is $346 \pm 14 \text{ mA h g}^{-1}$ during lithiation at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$, which compares well with the theoretical capacity. The specific capacity remains in excess of 300 mA h g^{-1} at $i_{\text{sp}} = 25 \text{ mA g}^{-1}$ and only drops off substantially at $i_{\text{sp}} = 100 \text{ mA g}^{-1}$, falling to $136 \pm 7 \text{ mA h g}^{-1}$. Nevertheless, the cell in the Spacer configuration can be cycled with adequate capacity up to 50 mA g^{-1} , compared to just 10 mA g^{-1} in

the Standard configuration. This has important consequences for *operando* Raman spectroscopy—not only are these higher currents more representative of those occurring within a practical electrochemical energy storage system, but faster currents also open up the possibility of performing more cycles on a practical timescale, and therefore afford the opportunity to study degradation and decomposition processes over multiple cycles¹⁸ rather than just reflecting the mechanism of the first few cycles. It is also worth noting that the error bars (standard deviation of measurements of multiple independently assembled cells) are significantly higher at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$ for the Standard over the Spacer configuration, further highlighting the increased reliability of the novel configuration.

In addition to the overall average capacities, differential capacities of representative graphite electrodes in the two configurations plotted against cell potential are shown in Figs. 4c and 4d. The differential capacity peaks for the Standard configuration (Fig. 4c) are poorly resolved, particularly at high i_{sp} ; this is consistent with the observed trends from simulation in Fig. 3, in which the poorer resolution of the dQ/dE response was correlated directly to a spatially inhomogeneous degree of lithiation across the electrode. We attribute the experimentally observed broadening of the dQ/dE response to the same phenomenon, i.e. inhomogeneous lithiation of the working electrode. In the case of the Spacer configuration, the resolution of the peaks for the lithiation and delithiation processes is much improved, particularly at $i_{\text{sp}} = 10$ and 25 mA g^{-1} . Consistent with the simulated dQ/dE plots, this suggests that each lithiation

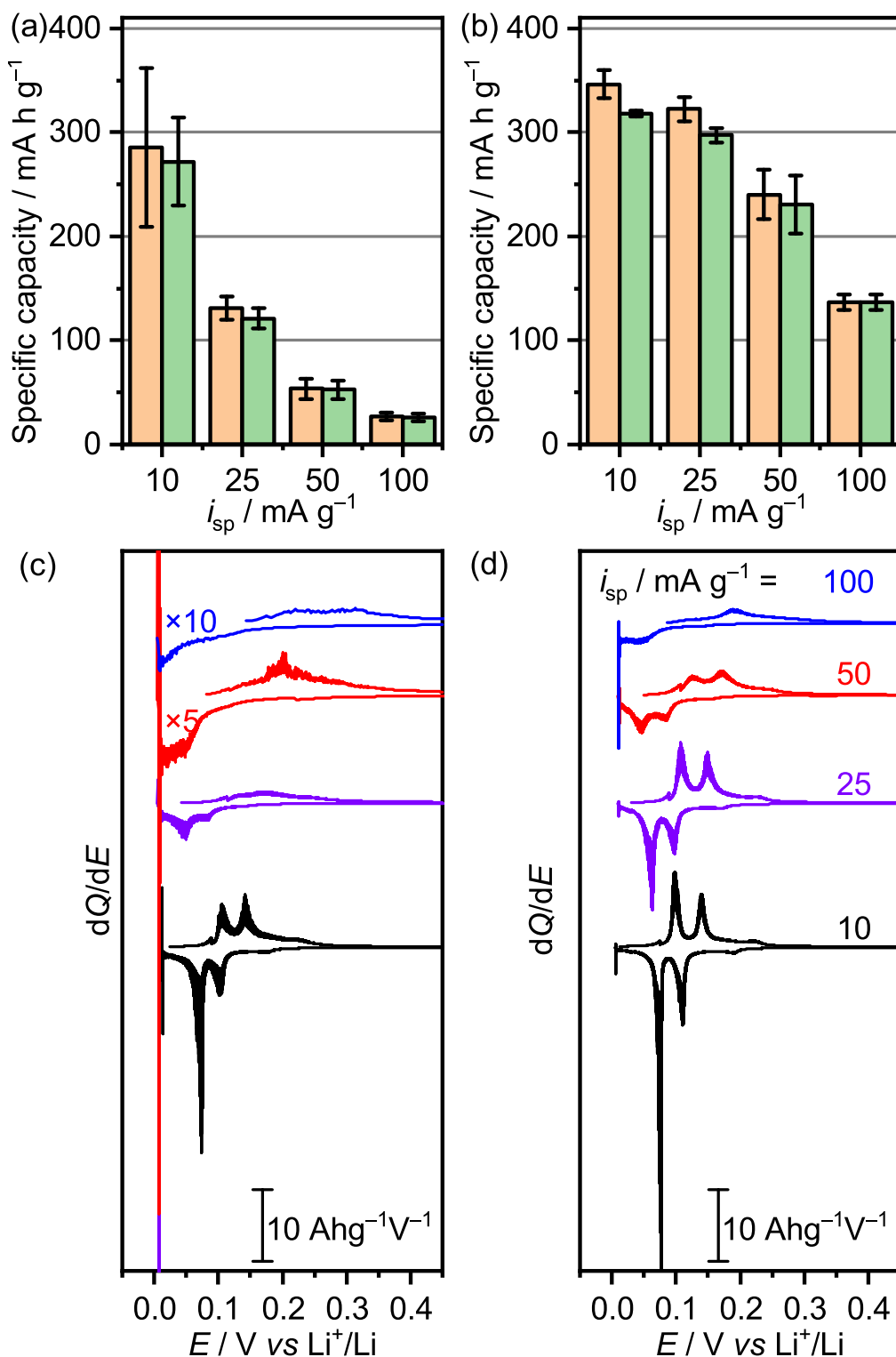


Figure 4. Average specific capacities during lithiation (orange) and delithiation (green) of graphite electrodes in (a) Standard and (b) Spacer configurations at specific currents from 10 to 100 mA g⁻¹. Data correspond to the first four charge-discharge cycles of the cell. Representative differential capacity plots of graphite electrodes in (c) Standard and (d) Spacer configurations at specific currents of 10 (black line), 25 (purple), 50 (red) and 100 (blue) mA g⁻¹.

process occurs within a narrow potential range across the entire electrode, and therefore a Raman spectrum of any one location will be more representative of the condition of the whole sample at that SOC, giving improved confidence in the results.

It should be noted that the experimental differential capacity plots exhibit the closest quantitative correspondence to the simulation predictions when the real (measured) compressed spacing separator

thickness of 70 μ m in the experimental system is increased to a 250 μ m thickness in the simulation. We emphasize that the simulation was undertaken for the purpose of qualitative insight, identifying potentially promising *operando* cell configuration before time-consuming but necessary experimental validation. The discrepancies may arise from material non-uniformity in the electrode or separator, the presence of a small volume of free electrolyte between the

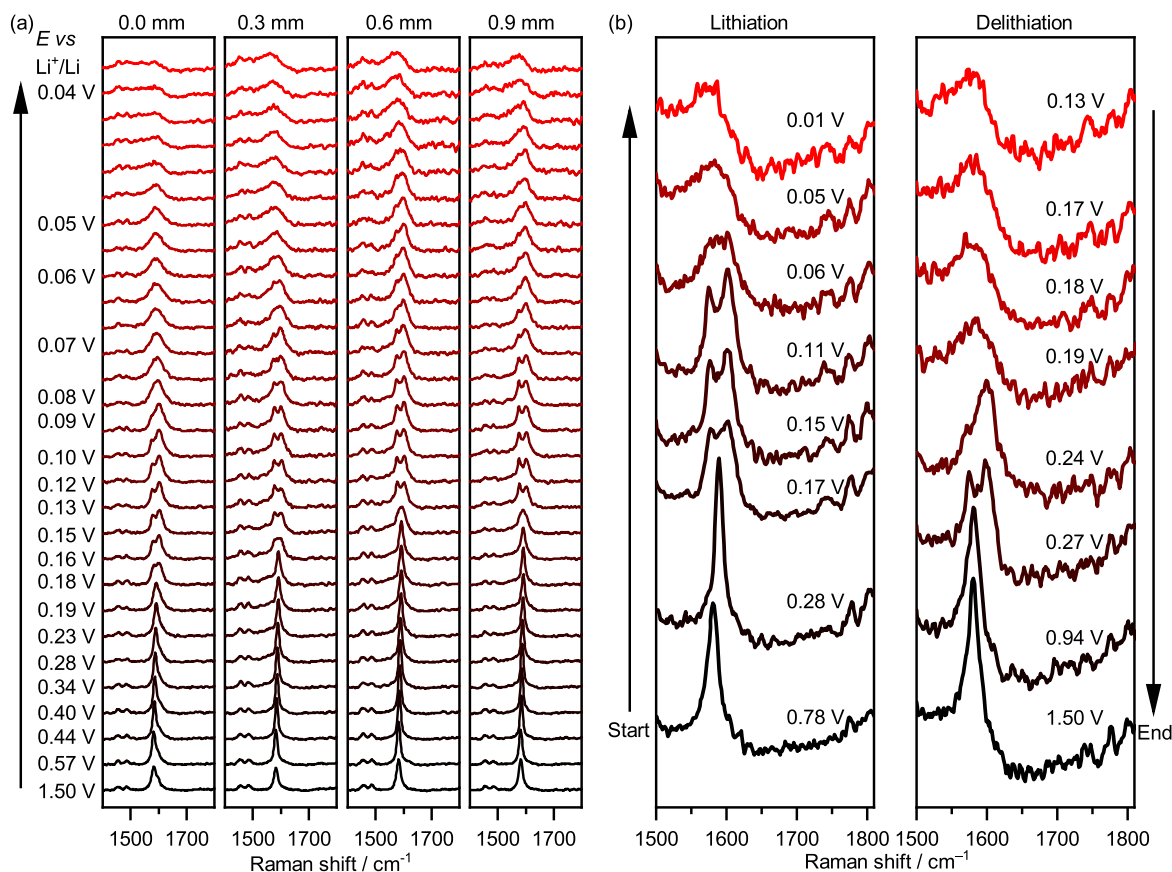


Figure 5. Operando Raman spectra of graphite electrodes in (a) Standard configuration during lithiation at $i_{\text{sp}} = 10 \text{ mA g}^{-1}$, at specified distances from the electrode edge to demonstrate the spatial non-uniformity of the response and (b) Spacer configuration at the center of the electrode ($= 0.75 \text{ mm}$ from the electrode edge) at $i_{\text{sp}} = 25 \text{ mA g}^{-1}$. Spectra in parts (a) and (b) are plotted on different intensity scales.

separator(s) and/or interactions with the window improving electrolyte diffusion compared to the model, or due to general imprecision in the assumed material properties for the system, which were sourced from literature and were not fitted independently to the experimental data presented here. Nonetheless, the overall trends with respect to the two configurations are consistent between experiment and theory.

Operando Raman spectroscopy of graphite electrodes for Li-ion batteries.—Spatially-resolved operando Raman spectroscopy was performed both to corroborate the significant difference in performance in terms of lithiation homogeneity and overall capacity between the Standard and Spacer cell configurations suggested by modeling and electrochemical characterization, and to demonstrate the quality of Raman spectra that could be obtained in the new configuration. The Raman spectrum of graphite is dominated by the “G” (graphitic) peak at 1580 cm^{-1} , which is very sensitive to lithium intercalation processes and therefore provides a suitable probe for the variation in this property both spatially and as a function of potential.³⁴ During the initial stages of lithiation of graphite negative electrodes, the G peak shifts to higher wavenumber (1600 cm^{-1}) and sharpens, before splitting into two at approximately 0.2 V vs Li^+/Li , broadening into one peak at approximately 0.1 V vs Li^+/Li and finally disappearing altogether at potentials approaching 0 V vs Li^+/Li .^{10,17}

The photograph in Fig. S1 and the modeling predictions in Fig. 2 suggest that the Standard configuration exhibits a large degree of lithiation inhomogeneity. To confirm this experimentally, operando Raman spectra were recorded at different distances from the edge of the graphite working electrode strip in Standard configuration during galvanostatic lithiation at 10 mA g^{-1} , and the results are shown in Fig. 5. For Raman spectra recorded at the electrode edge ($0 \mu\text{m}$), the

well-characterized spectral transitions described above were observed at potentials matching the literature. However, towards the electrode center and particularly at distances of $>600 \mu\text{m}$ from the edge of the electrode, the transition from a single to a split G peak was not observed until potentials 50 mV more negative than those at the edge. This indicates a measurable lag in lithiation in the central region compared with the electrode edge, as predicted by the modeling shown in Fig. 2, even at a very low specific current of 10 mA g^{-1} . This makes it dangerous to draw conclusions from operando Raman spectroscopy using this configuration as the data will be very sensitive to the precise location on the electrode-window interface where the Raman spectrum is measured and any spatial inhomogeneity intrinsic to the electrode sample itself cannot be resolved from that caused by the specific geometry.

Electrochemical characterization of graphite electrodes in the Spacer configuration demonstrates that, unlike for the Standard configuration, acceptable specific capacity and well resolved differential capacity peaks can be obtained at $i_{\text{sp}} \leq 50 \text{ mA g}^{-1}$. Therefore, operando Raman spectroscopy was performed at the center of a graphite working electrode strip in the Spacer configuration, cycling at 25 mA g^{-1} (Fig. 5b). These spectra display the characteristic spectral transitions during lithiation at potentials matching literature examples,¹⁰ and also during delithiation but with some hysteresis, as observed in the differential capacity/potential plots in Fig. 4d. This shows that it is possible to obtain satisfactory operando Raman spectra in the new configuration at an increased i_{sp} of 25 mA g^{-1} . Additionally, to verify the improved spatial lithiation homogeneity predicted above for the Spacer configuration, operando Raman spectra were recorded from different locations on the electrode exposed by the holed spacing separator at a potential of 0.08 V vs Li^+/Li (Fig. S4). These spectra are effectively indistinguishable, demonstrating improved spatial homogeneity of lithiation in the

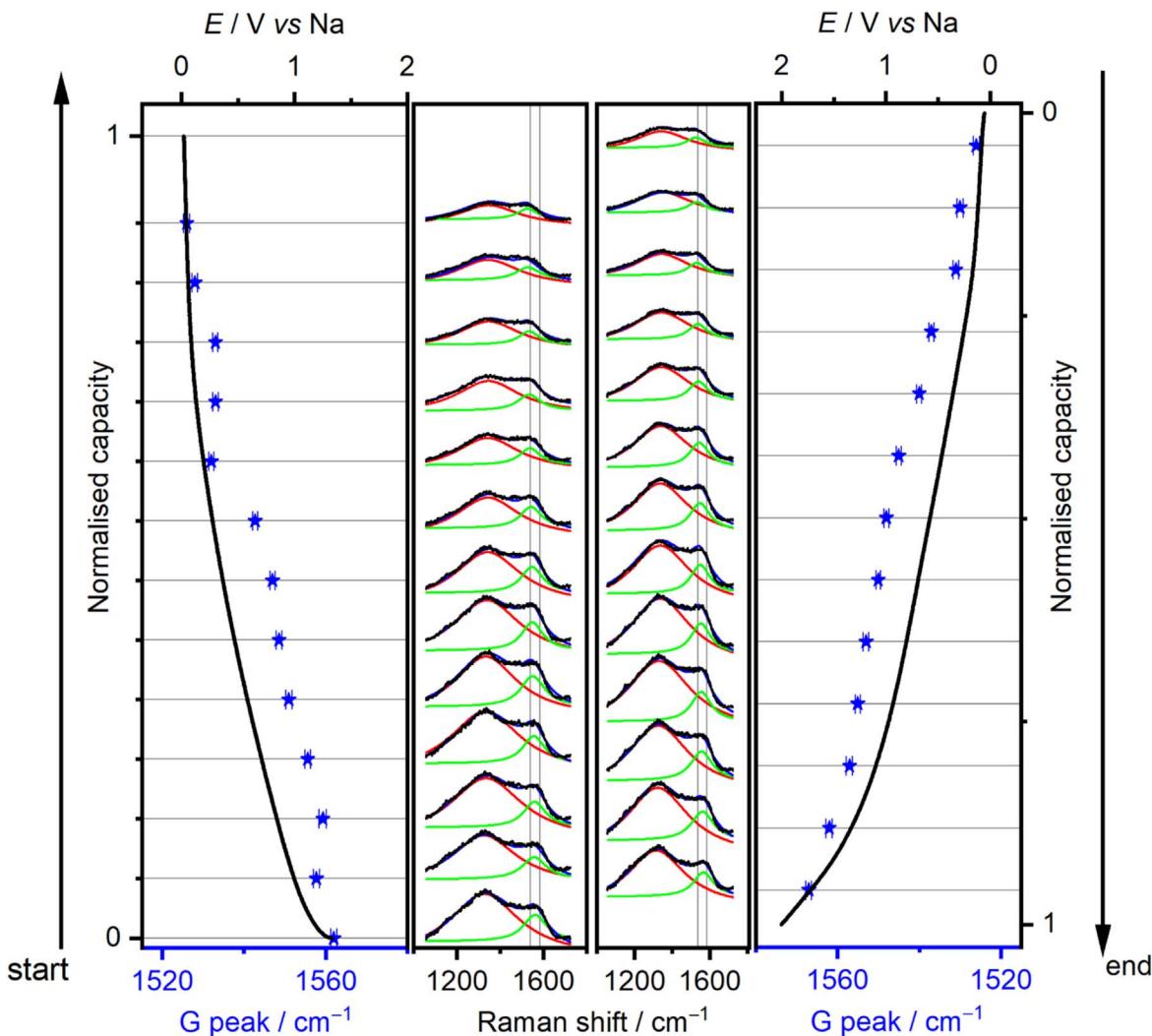


Figure 6. *Operando* Raman spectroscopy of hard carbon anode in Spacer configuration at $i_{sp} = 25 \text{ mA g}^{-1}$ using a 785 nm laser. Raman peaks were fit using Lorentzian lineshapes. The plotted data in this case correspond to the fourth charge/discharge cycle so capacities are normalized to the specific capacity measured for the associated sodiation (168 mA h g^{-1}) and desodiation (163 mA h g^{-1}).

Spacer configuration. These results corroborate the above predictions and observations surrounding the improved spatial homogeneity of lithiation for the Spacer configuration compared to the Standard configuration, and confirm that a spectrum measured at a single location can be safely considered representative of the whole electrode. The spacing separator may also offer the advantage of removing the chemical influence of the sapphire window from immediate contact with the electrode, replacing it with a glass fiber separator that offers a well-characterized chemical environment.³⁵

It is apparent, however, that the additional $70 \mu\text{m}$ layer of electrolyte solution required to allow electrolyte access to the electrode reduces the signal-to-noise ratio of the spectra in Fig. 5b compared to Fig. 5a (presented after removal of the fluorescence background). In the case of the relatively intense G peak associated with graphite, this does not result in the loss of spectral detail, and thus the higher cycling currents obtained in the Spacer configuration justify the minimal loss of spectral signal-to-noise. However, it should be borne in mind that for electrodes exhibiting very weak Raman scattering, low signal to noise of the Raman signal may necessitate the use of a narrower spacing separator and longer acquisition times, and therefore lower specific currents. We also note that the need to perform a background subtraction from the spectra indicates that electrolyte fluorescence may still be problematic at the $70 \mu\text{m}$ path length used, although this will be strongly dependent on

the electrolyte chemistry. Alternative strategies for maintaining and improving the rate capability of *operando* Raman cells whilst minimizing the distance through which the Raman light must pass, such as through the use of optical fibers, are currently being explored, although the sole use of standard and commercially-available components with no need for modification offers a significant advantage of the presented configuration for laboratory use.

Operando Raman spectroscopy of hard carbon electrodes for Na-ion batteries.—To demonstrate the broad applicability of the Spacer configuration for *operando* Raman spectroscopic studies on electrochemical energy storage devices, the Na-ion storage properties of a hard carbon electrode were investigated. Hard carbon is an established negative electrode active material for sodium-ion batteries, and operates by a reversible adsorption/insertion mechanism.^{20,31,36,37} Strips of hard carbon active material on an Al foil current collector were cycled in 1 mol kg^{-1} NaTFSI in PC electrolyte solution. The Raman spectrum of the hard carbon electrodes displays typical carbon D (1350 cm^{-1}) and G (1580 cm^{-1}) peaks. These peaks are much broader than those observed for graphite (see Fig. 5), indicating a more amorphous, disordered structure.³⁸ During sodiation, the G peak shifts from 1580 cm^{-1} to 1520 cm^{-1} in the fully sodiated state at $0.02 \text{ V vs Na}^+/\text{Na}$; this process is reversed upon desodiation

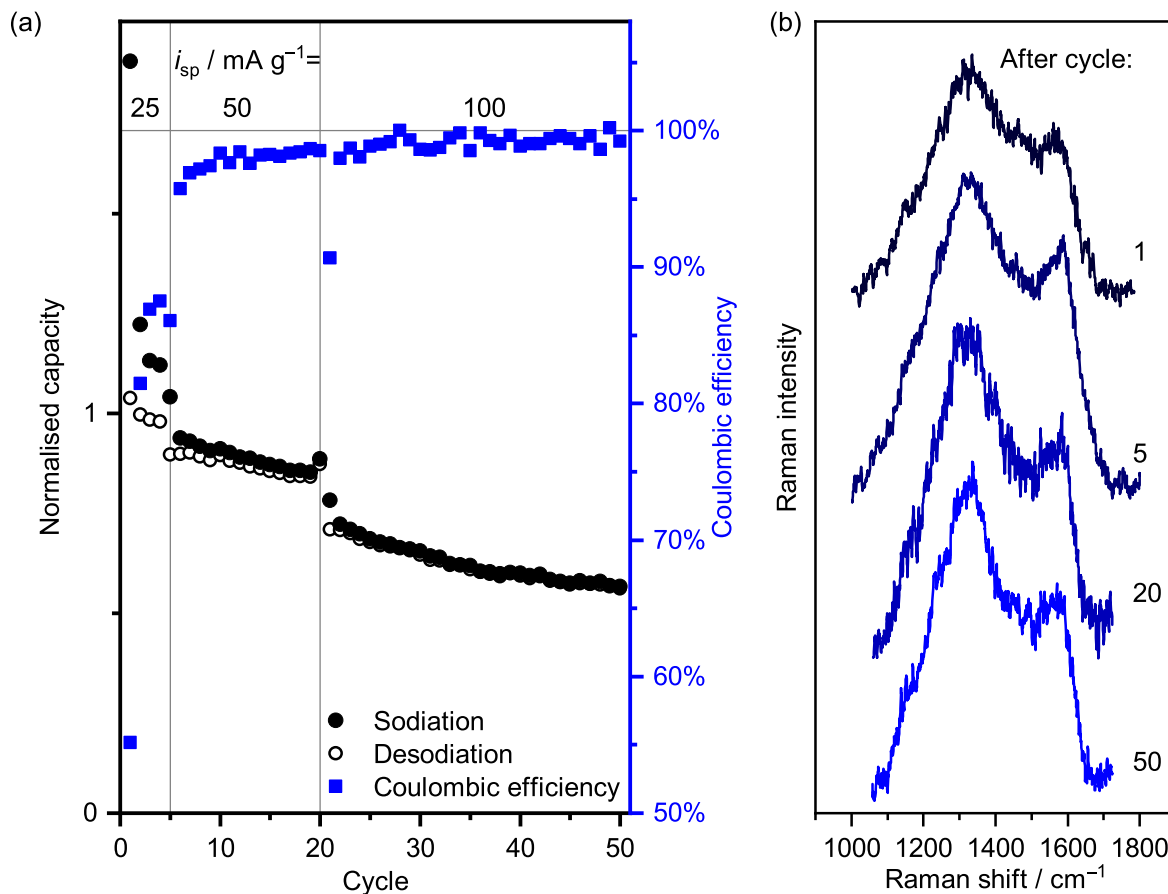


Figure 7. (a) Specific capacity and coulombic efficiencies of hard carbon electrode cycled in 1.0 mol kg⁻¹ NaTFSI in PC at specific currents of 25, 50 and 100 mA g⁻¹ in Spacer configuration (capacities normalized to the second cycle desodiation capacity, in this case measured as 243 mA h g⁻¹). (b) *In situ* Raman spectra of the electrode at SOC = 0 after 1, 5, 20 and 50 cycles.

(Fig. 6). This behavior is in accordance with literature studies,^{39,40} and again demonstrates that the new cell configuration is able to resolve spectral changes at increased specific currents.

A particular advantage of cycling at significantly higher currents than achievable in the Standard configuration is the ability to perform many cycles at realistic rates in an experimentally practical amount of time. The hard carbon electrode was subjected to sodiation/desodiation for 5 cycles at $i_{sp} = 25$ mA g⁻¹, 15 cycles at $i_{sp} = 50$ mA g⁻¹ and finally 30 cycles at $i_{sp} = 100$ mA g⁻¹, with the relative capacities and coulombic efficiencies shown in Fig. 7a. After the first 5 cycles, the coulombic efficiencies are well in excess of 95%. Increasing the specific current from 25 to 50 mA g⁻¹ results in only a negligible loss in capacity, and from $i_{sp} = 50$ to 100 mA g⁻¹ the loss is approximately 15% initially, which is less than the loss observed with graphite electrodes in Fig. 4b, although still believed to be due to diffusion limitations at high specific currents as predicted by electrochemical modeling. Cycling at 100 mA g⁻¹ results in a 20% loss in capacity between cycles 21 and 50, which is more severe than found studying the same electrodes in a “face-to-face” lab-scale cell configuration without a Raman window (Fig. S5). A graphite electrode was also cycled in a lithium-ion Spacer configuration cell (Fig. S6) at 50 mA g⁻¹, and a comparable 25% loss of specific capacity from cycle 1 to cycle 30 is observed. Therefore, it appears that similar capacity fade over tens of cycles is observed for the Spacer configuration using both hard carbon and widely-used graphite electrodes. This fade is therefore probably associated with the cell design, potentially caused by factors such as oxygen or moisture ingress, although some capacity fade is expected during the early cycles of a graphite-containing Li ion cell even under more optimized pouch cell conditions.^{41,42} Figure 7b shows Raman spectra recorded after increasing numbers of cycles, focusing

on the Raman peaks. In this case, no significant change in the D and G hard carbon peaks is observed after 50 cycles. The ability to perform tens and in future hundreds of cycles in the *operando* Raman cell opens up the possibility of studying materials degradation mechanisms under near-equivalent conditions to a standard laboratory cell test. Further optimization of the Spacer configuration cell design, particularly around more effective sealing strategies, should be possible in order to minimize capacity fade arising from external environmental factors.

Conclusions

We have presented a significant improvement on an established cell configuration for performing *operando* Raman spectroscopy on coated metal foil electrodes used for electrochemical alkali-ion storage. The Raman cell is prepared by spacing the electrode face from the cell window using an additional separator, allowing improved electrolyte access to the entire surface of the electrode, and therefore improved electrochemical performance and greater confidence in the Raman spectra obtained. This configuration was predicted by modeling to significantly improve the spatial homogeneity of lithiation of the working electrode, and was validated experimentally on a commercially-sourced graphite electrode. Moreover, the new configuration delivers improved electrochemical performance at higher specific currents as assessed from specific capacity and differential capacity measurements. The modification to the existing state-of-the-art recommended in this work enables cycling conditions in Raman cells that are more representative of those used in electrochemical screening of battery electrodes. Finally, the higher specific currents accessible from the new configuration allow up to five times more cycles to be performed in a given time compared to the previous approach, such that

degradation mechanisms can be studied across tens to hundreds of cycles. We stress that, due to the wide range of alternative cell designs, test conditions and materials presented in the literature, a broader comparison with these configurations is not possible. Nevertheless, the concept of the Spacer configuration may be extended to such alternative cells to allow their further optimization.

More broadly, this study underlines that cell modifications necessary to perform *operando* spectroscopic measurements on electrode materials can have detrimental effects on the electrochemical performance of the cell, which in severe cases may invalidate conclusions drawn from such measurements when applied to more conventional cell configurations. Therefore, we advocate a design framework based upon modeling of the electrochemical performance of the spectroscopic cell in its particular modified configuration, followed by experimental validation of overall gravimetric capacity and differential capacity across a range of specific currents, prior to undertaking spectroscopic measurements. When successful, this methodology provides essential confidence that observations about electrode material chemistry and mechanisms inferred from *operando* Raman spectroscopy can be applied in technological development of commercial electrochemical energy storage devices.

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ORCID

Edmund J. F. Dickinson  <https://orcid.org/0000-0003-2137-3327>

Rinaldo Raccichini  <https://orcid.org/0000-0003-1507-2739>

Gareth Hinds  <https://orcid.org/0000-0002-8925-188X>

Andrew J. Wain  <https://orcid.org/0000-0002-8666-6158>

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