Nature of the Cathode–Electrolyte Interface in Highly Concentrated Electrolytes Used in Graphite Dual-Ion Batteries

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ABSTRACT: Dual-ion batteries (DIBs) generally operate beyond 4.7 V vs Li+/Li0 and rely on the intercalation of both cations and anions in graphite electrodes. Major challenges facing the development of DIBs are linked to electrolyte decomposition at the cathode–electrolyte interface (CEI), graphite exfoliation, and corrosion of Al current collectors. In this work, X-ray photoelectron spectroscopy (XPS) is employed to gain a broad understanding of the nature and dynamics of the CEI built on anion-intercalated graphite cycled both in highly concentrated electrolytes (HCEs) of common lithium salts (LiPF6, LiFSI, and LiTFSI) in carbonate solvents and in a typical ionic liquid. Though Al metal current collectors were adequately stable in all HCEs, the Coulombic efficiency was substantially higher for HCEs based on LiFSI and LiTFSI salts. Specific capacities ranging from 80 to 100 mAh g−1 were achieved with a Coulombic efficiency above 90% over extended cycling, but cells with LiPF6-based electrolytes were characterized by <70% Coulombic efficiency and specific capacities of merely ca. 60 mAh g−1. The poor performance in LiPF6-containing electrolytes is indicative of the continual buildup of decomposition products at the interface due to oxidation, forming a thick interfacial layer rich in LiPF6, PO4,F−, LiPO2,F− and organic carbones as evidenced by XPS. In contrast, insights from XPS analyses suggested that anion intercalation and deintercalation processes in the range from 3 to 5.1 V give rise to scant or extremely thin surface layers on graphite electrodes cycled in LiFSI- and LiTFSI-containing HCEs, even allowing for probing anions intercalated in the near-surface bulk. In addition, ex situ Raman, SEM and TEM characterizations revealed the presence of a thick coating on graphite particles cycled in LiPF6-based electrolytes regardless of salt concentration, while hardly any surface film was observed in the case of concentrated LiFSI and LiTFSI electrolytes.

KEYWORDS: graphite, anion intercalation, concentrated electrolyte, cathode–electrolyte interface, photoelectron spectroscopy, battery

1. INTRODUCTION

The increasing need to harness renewable energy sources has created a necessity for safe and cost-effective energy storage systems that are suited for large-scale stationary use. Typical examples of battery chemistries employed in such applications include lead-acid, nickel–cadmium, nickel–metal hydride, sodium–sulfur, and redox flow batteries.1,2 Among the emerging technologies that are considered promising for stationary energy storage are dual-ion batteries (DIBs)3,4 and in particular graphite dual-ion batteries (GDIBs).5 GDIBs offer a maximum capacity of ~140–150 mAh g−1; combining this with a high operational voltage (~4.5 V vs Li+/Li0) and an optimized cell design results in a competitive energy density ranging from 210 to 260 Wh L−1.5,6 The energy density is lower compared to most Li-ion systems (~400 Wh L−1), but is compensated by the environmental and cost benefits associated with GDIBs, as the use of expensive transition metal oxides can be eliminated and cheaper resources can be used.4,6

The mechanism of charge storage in the positive electrode in GDIBs relies on the reversible intercalation of anions into the layered structure of graphite.Graphite is oxidized during charge accompanied by anion intercalation, as shown by eq 1.

\[ xA^− + \text{Graphite} \leftrightarrow A_x\text{Graphite} + xe^− \] (1)

\[ xLi^+ + xe^- + \text{Graphite} \leftrightarrow Li_x\text{Graphite} \] (2)

In eq 1, “A−” stands for the anion intercalant such as PF6−, FSI, or TFSI. When discharging, the DIB cell undergoes the reverse reactions leading to recombination of anions and cations in the

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Studies on anion intercalated graphite have been well-documented, and the operating mechanism of GDIBs was patented already in 1989 by McCullough et al.11 However, the practical application of these devices is still under development. Operational challenges are associated with the unusually high working voltage (>4.4 vs Li+/Li0) required for anion intercalation and the poor reversibility of anion intercalation in graphite. Common electrolytes used in lithium-ion batteries consist of carbonate solvents which are prone to decomposition beyond 4.0 V, resulting in a poor Coulombic efficiency (<90%) and capacity retention in GDIBs.12 Solvents prone to oxidation aggravate self-discharge, making the long-term storage of charged GDIBs problematic.73 Further limitations include structural degradation associated with the irreversibility of the anion intercalation and solvent co-intercalation into the graphite positive electrode,34 as well as corrosion of the Al current collector.15 A number of approaches have, however, been proposed to increase the stability and lifetime of GDIBs. Notably, studies have focused on the use of (1) small, planar anion intercalants,16,17 (2) electrolyte solvents unlikely to cointercalate in the graphitic cathodes,18 (3) concentrated electrolytes and ionic liquids,8,10 (4) surface-passivating additives,19−21 and (5) morphological tailoring of the graphite positive electrode.22−24

While the nature of the cathode–electrolyte interphase (CEI) has been investigated for transition metal oxide (TMO) cathodes in commercial electrolytes (for example, 1 M LiPF6 in EC/DEC),25,26 few similar studies exist for GDIBs. For instance, Li et al. designed an interphase layer on the graphite positive electrode by cycling in the voltage range of 0.3−2.0 V versus Li+/Li0 in 1 M LiPF6 in ethyl methyl carbonate (EMC).27 Such modification of the CEI resulted in a 12% increase in the specific capacity and a capacity retention of >98% over 2000 cycles. This highlights the importance of using CEI-generating electrolyte additives for improving the performance of GDIBs.

The stability of the Al current collector is also critical when used together with high voltage cathodes (>5.0 V vs Li+/Li0).28 Commercial electrolytes are based on LiPF6, which inhibits Al corrosion through the buildup of an ALF3 passivating layer, a process triggered by anion decomposition.29 However, the reactivity of the PF6− anion and its high sensitivity to traces of moisture30 make LiPF6 an unlikely candidate for use in GDIBs. More chemically stable lithium salts, such as LiN(SO2F)2 (LiFSI) and LiN(SO2CF3)2 (LiTFSI), have demonstrated higher oxidative stability and a more reversible anion intercalation into graphite. In contrast, these salts aggravate the corrosion of the Al current collector. The current collector degradation has been attributed to pitting corrosion initiated by Cl− impurities, frequently present in these salts,31,32 and to anodic dissolution, as the native Al2O3 layer reacts with the anions, forming the soluble complexes ([Al(FSI)3]− and [Al(TFSI)3]−).33 Recent studies have demonstrated that the stabilization of the Al current collector can be achieved in concentrated electrolytes consisting of LiFSI/LiTFSI salts in carbonate solvents and in ionic liquids, as the solubility of the AlF3 complexes decreases significantly in the absence of coordinating solvent molecules.34,35

This work aims to understand the nature of the CEI in GDIBs using X-ray photoelectron spectroscopy (XPS). Experiments have been performed on two types of electrodes based on highly ordered pyrolytic graphite (HOPG) and microcrystalline KS6 graphite. The monolithic HOPG was cycled in 1 M LiFSI in Pyr14FSI (1-butyl-1-methylpyrrolidinium bis-(fluorosulfonylimide)) and served as a model system for analysis of anion-intercalated graphite in the absence of solvent decomposition products, carbon black, and binder. The composite graphite electrodes (composed of KS6 graphite, carbon black, and CMC binder) were cycled in both dilute and concentrated solutions of LiPF6, LiFSI and LiTFSI in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), as well as in an ionic liquid electrolyte (1 M LiFSI in Pyr14FSI). Surface characterizations of the electrodes, in their charged and discharged states, were undertaken using in-house XPS to gain insight into the nature and evolution of the CEI. It is expected that these results will benefit efforts to design long-life GDIBs through artificially created, thin CEI layers that are selectively permeable to anions.

2. EXPERIMENTAL SECTION

2.1. Cell Preparation. 2.1.1. Electrode Fabrication. Two types of graphite-positive electrodes were prepared, based on either monolithic HOPG (Agar Scientific) or KS6 graphite (Timcal, Imerys). HOPG was used since it is nearly ideal as substrate for XPS studies. KS6 was employed due to its promising electrochemical performance in GDIBs. The HOPG was cut into electrode pieces (approximately 5 mm × 5 mm × 2 mm in size) with a scalpel, dried at 120 °C for 12 h under vacuum, and stored in an Ar-filled glovebox (O2 < 1 ppm, H2O < 1 ppm). Composite electrodes were prepared from a slurry consisting of 90% graphite, 6% Super P carbon (Alfa Aesar), 4% sodium carbomethyl cellulose (CMC, Leclanché), and 3 mL of a 9:1 solution of deionized water and ethanol, which was homogenized using a Vortex Genie2 mixer. The slurry was cast onto carbon-coated Al foil (MTI) and dried at ambient condition. Electrode disks with a diameter of 13 mm were punched, dried at 120 °C over 12 h under vacuum, and stored in an Ar-filled glovebox. Li disks (Cyprus Foote Mineral) with a diameter of 15 mm were used as the counter and reference electrodes.

2.1.2. Electrolyte Preparation. Three types of salts, namely, LiPF6 (Alrich, >99.9%), LiTFSI (BASF), and LiFSI (Suzhou Fluolyte, >99.9%) were dissolved in a 1:1 (v/v) EC (Gotion)/DEC (Gotion) solvent mixture to prepare electrolytes with concentrations of 1, 2, and 4 M. The salts dried in a vacuum oven at 120 °C for 12 h and stored in an Ar-filled glovebox (O2 < 1 ppm, H2O < 1 ppm). The electrolyte solvent was dried over molecular sieves for at least 48 h (resulting in H2O content < 1 ppm) and filtered through 200 nm PTFE membranes prior to mixing with the salt. To prepare the concentrated electrolytes, the solutions were heated to 60 °C for LiTFSI and LiFSI and to 45 °C in the case of LiPF6. An electrolyte based on ionic liquid with the formulation 1 M LiFSI in Pyr14FSI (Solvionic) was also considered in this study. The H2O content in the LiFSI- and LiTFSI-based electrolytes was determined using a 756 Karl Fischer coulometer (Metrohm) and varied between 15 and 60 ppm depending on the electrolyte concentration. The LiPF6-based electrolytes and the 1 M LiFSI in Pyr14FSI showed a water content below 2 ppm. All electrolyte preparation took place in the glovebox.

2.1.3. Cell Fabrication. Pouch cells were assembled using a KS6 graphite cathode as the working electrode and a 26 mm glass fiber separator (240 μm thick, Whatman) impregnated with 150 μL of electrolyte. The counter and reference electrodes consisted of metallic Li, and the experiments took place in a two-electrode half-cell format, unless otherwise stated. The final sealing pressure was 5 mbar. All cells containing the ionic liquid and the highly concentrated 4 M

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Electrolytes were put in an oven at 55 °C for 20 min prior to electrochemical testing in order to ensure proper electrode wetting. The setup for the cells with an HOPG positive electrode was identical, with the only difference being that these were impregnated with 300 μL of electrolyte, due to the high electrode mass and thickness.

2.2. Electrochemical Characterization. Electrochemical testing was conducted using cyclic voltammetry and galvanostatic test protocols on MPG2 Biologic potentiostats and an Arbin BT cycler. Cyclic voltammograms were acquired at a scan rate of 0.050 mV s⁻¹ and most chronopotentiometric measurements were conducted at a charge/discharge current of 10 mA g⁻¹ of active material. HOPG electrodes were cycled with a lower charge/discharge current of 1 mA g⁻¹. Spectroscopic and microscopic characterizations were performed for the galvanostatically cycled cells, unless otherwise stated.

2.3. X-ray Photoelectron Spectroscopy. 2.3.1. XPS on Monolithic Highly Oriented Pyrolytic Graphite Electrodes. To establish a basic understanding of the positive interface in GDIBs, initial XPS measurements were performed on HOPG electrodes. The elimination of the conducting additive and binder facilitated the spectral interpretation. HOPG electrodes were galvanostatically cycled (at 1 mA g⁻¹) against Li and in 1 M LiFSI in Pyr14FSI, to avoid C 1s contributions from the salt and/or carbonate solvents.

Figure 1. Anion intercalation in KS6 graphite from (a) 1 M LiPF₆ in EC/DEC, (b) 4 M LiPF₆ in EC/DEC, (c) 4 M LiTFSI in EC/DEC, (d) 4 M LiFSI in EC/DEC, and (e) 1 M LiFSI in Pyr14FSI. The designated redox peak potentials correspond to the first CV cycle. In (f), evolution of the current onset potential during cycles 1, 2, and 10.
Spectra of the pristine, electrolyte soaked, fully charged (5.1 V vs Li+/Li⁰), and fully discharged (3.0 V vs Li+/Li⁰) HOPG (basal plane) were acquired to understand the effect of state-of-charge. The “soaked” samples were assembled in half-cell format and left to rest for 24 h prior to disassembly. Before analysis, the HOPG electrodes were cleaved (by carefully applying pressure with a scalpel on the 2 mm thick side), and no washing procedures were used. The freshly exposed surface was used for the analysis. All samples were handled under a glovebox atmosphere and brought to the spectrometer (PHI 5500) in an airtight transfer shuttle. Monochromatic Al Kα radiation was used for the measurements (hv = 1486.7 eV) at an emission angle of 45°. Fitting was performed with Igor Pro (v. 6.37), using a Gaussian/Lorentzian mixed line shape after the subtraction of a Shirley background. The N 1s peak belonging to nongrounded, graphite grids (with holey carbon as the current collector, redispersed in DMC and sonicated for 30 min. A drying at ambient conditions, the composite lms were removed from the current collector, dispersed in DMC and sonicated for 30 min. A few (2 to 3) drops of the dispersions were deposited on the TEM grids (with holey carbon lms on top) and transferred to the microscope without exposure to air.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Anion Intercalation and Associated Structural Changes. The cyclic voltammograms (CV) in Figure 1 revealed the inherent dependence of the reversibility and kinetics of electrochemical anion intercalation on the chemical nature of the anion and its concentration in the electrolyte. Anion characteristics such as charge density, ionic size, stereochemistry, and solvent coordination determine the ease of intercalation into the graphitic host, usually manifested in the onset overpotential. Here, the intercalation overpotential during the first charge decreased in the order PF⁶⁻ > FSI > TFSI. Generally, the species with a smaller ionic radius and a higher charge density such as PF⁶⁻ and FSI could be subjected to stronger interactions with solvent molecules and Li⁺ compared to TFSI, hence exerting an increased drag force in the electrolyte. The impact of the anion drag force on the intercalation overpotential could be seen clearly by comparing the 4 M LiFSI in EC/DEC system to the 1 M LiFSI in Pyr14FSI system. The latter exhibits an overpotential almost 0.2 V higher than the former (4.57 vs 4.37 V vs Li+/Li⁰), owing to the absence of a conventional solvent in the ionic liquid. In this case, FSI is surrounded by 1-butyl-1-methylpyrrolydinium cations (instead of neutral solvent molecules such as EC and DEC), hence increasing the resistance against intercalation in graphite. The marked increase in intercalation overpotentials in both 1 and 4 M LiPF⁶ (4.72 and 4.76 V vs Li+/Li⁰, respectively) could be due to the formation of a thick interphase on the positive graphite electrode, leading to concentration polarization across the CEI and impedance of anion intercalation. The poor reversibility exhibited by the dual-ion cell (Figure 1a,b) was particularly pronounced in the case of 4 M LiPF⁶, where an asymmetry in the oxidation and reduction peaks was observed along with a large peak-to-peak voltage difference. Moreover, the majority of the anions were de-intercalated below 4.0 V, which could be indicative of inefficient ion conduction across the CEI layer. In 4 M LiTFSI and 4 M LiFSI electrolytes (Figure 1c,d), anion cycling occurred more readily and reversibly as demonstrated by the low onset overpotential. Multiple redox peaks appeared during both anion intercalation and deintercalation as different graphite intercalation compounds (GICs) formed. Anion intercalation from the 4 M LiFSI in EC/DEC showed similar characteristics to the 4 M LiTFSI in EC/DEC electrolyte. It should, however, be noted that anion extraction appeared to be more sluggish and that the majority of anions could be released into the electrolyte below 4.4 V vs Li+/Li⁰. This could be attributed to the higher charge density of the FSI anion that caused a stronger interaction with the graphite host. In the ionic liquid electrolyte (Figure 1e), a similar phenomenon was noted but with substantially higher overpotential for deintercalation. Apart from the high charge density, the impaired kinetics of FSI anion intercalation/deintercalation in the ionic liquid could further be ascribed to the high viscosity and possibly the ion pairing which decreased the ionic conductivity. Spectroscopic evidence confirming the reversible anion intercalation for the electrolyte systems studied is provided in Figure S26, which shows the Raman spectra of fully charged/discharged electrodes for cycles 1, 2, and 10. On the basis of the changes in the intensity of the defect (D band) and the intercalation component of the graphite band (D’ band), FSI intercalation was found to cause the least severe damages to the layered graphite structure, though both TFSI and PF⁶⁻ intercalations were also observed to be reversible. Despite the good electrochemical reversibility and the Raman data showing that the material was still highly graphitic after cycling, irreversible structural changes were observed for a selection of the cycled graphite cathodes studied through ex situ X-ray diffraction (XRD, Figure S27). Initially, the splitting of the (002) reflection located at 26.49° (3.4 Å) to the (00n+1) and (00n+2) components was observed, which provided further structural evidence of the anion intercalation and graphite expansion. At the end of the charge (5.1 V vs Li+/Li⁰), the (00n+1) reflection had shifted to 22.13° (4.0 Å), and the (00n+2) reflection shifted to 33.15° (2.7 Å) for graphite cycled in 4 M LiTFSI in EC/DEC (Figure S27a). Upon the subsequent discharge, the (00n+1) and (00n+2) decreased in intensity, and the 002 component reappeared at approximately its original position (26.45°). However, considerable broadening could be observed, which indicated that exfoliation and disorder increased, as a consequence of the graphite interlayer expansion. The overall trend was similar for graphite cathodes cycled in 4 M LiFSI in EC/DEC and 1 M LiFSI in Pyr14FSI (Figure S27b,c). This result remains to be conirmed with in situ XRD studies in the future.

Returning to the electrochemistry, significant differences were observed in the magnitudes of the background current recorded at the end of charge for the concentrated electrolytes.
According to these, the 4 M LiTFSI electrolyte appeared to be more stable than both the 4 M LiFSI and IL electrolytes. The background current at high potentials, normally linked to solvent decomposition and Al current collector corrosion, was lower for the 4 M LiTFSI case, even when the voltage was swept beyond 4.8 V. This is in line with results from the Al current collector stability test (Figure S1c−g), in which the 4 M LiTFSI electrolyte resulted in oxidative currents which were at least an order of magnitude lower compared to the other compositions based on sulfonimide salts. A maximum peak current of \( \sim 125 \mu \text{A cm}^{-2} \) was observed for the 4 M LiTFSI in EC/DEC system as opposed to 1 mA cm\(^{-2}\) recorded for the IL electrolyte. Nevertheless, it appeared that passivation of the current collector surface was achieved even in the 4 M LiFSI in EC/DEC and 1 M LiFSI in Pyr\(_{14}\)FSI electrolytes resulting in lower oxidative currents in the subsequent cycles (Figure S1d,g). The structural integrity of the Al current collector in these three electrolytes was confirmed using post-mortem SEM analyses performed after three CV cycles (Figure S13b,f,h), which revealed a surface very similar to that of pristine Al (Figure S13a). This was in contrast to the 1 M LiFSI and 1 M LiTFSI electrolytes that

![Figure 2. Galvanostatic charge-discharge profiles of KS6 graphite cycled in (a) 4 M LiPF\(_6\) in EC/DEC, (b) 4 M LiTFSI in EC/DEC, (c) 4 M LiFSI in EC/DEC and (d) 1 M LiFSI in Pyr\(_{14}\)FSI. (e) Associated gravimetric capacities. (f) Coulombic efficiencies for extended cycling.](https://dx.doi.org/10.1021/acsami.0c18586)
caused severe damage to the current collector in the form of corrosion pits as large as 100 μm (Figure S13e,g). In addition, the electrodes cycled in 4 M LiFSI/LiTFSI in EC/DEC and in IL remained largely unaffected as revealed in the SEM images taken after the 10th charge, apart from certain surface roughness and exfoliation of the cycled graphite particles (Figure S14a,b,e,f). This could be indicative of solvent decomposition in the electrode, resulting in the formation of “blisters.” Moreover, while the SEM/EDS of graphite electrodes cycled in concentrated 4 M LiFSI and 4 M LiTFSI provided no clear evidence of current collector corrosion (see Figures S14, S18, and S19), the corresponding SEM images for the IL electrolyte (Figures S14 and S15) revealed the presence of a decomposition product rich in Al and FSI and hence indicated that the IL was not equally passivating. Finally, a last point in favor of using the highly concentrated version of the LiFSI/LiTFSI in EC/DEC electrolytes was that the anion intercalation could barely be observed in the most dilute versions (1 M) of these electrolytes (Figure S2a,c). This was due not only to the side reactions taking place but also to the fact that a higher overpotential for anion intercalation was required in the dilute electrolytes, something that was confirmed by comparing these CVs to those of cells cycled at concentrations of 2 M (Figure S2b,d) and 4 M (Figure 1c,d).

Unlike the electrolytes based on LiFSI and LiTFSI, anion intercalation was observed even for the lower concentration 1 M LiPF6 electrolyte. Unique to the PF6− anion especially in the presence of EC, decomposition reactions helped form protective layers on both the current collector and graphite electrode. The good passivation of the Al current collector in LiPF6-containing electrolytes was reflected in the low oxidative currents recorded when sweeping the potential to 5.2 V vs Li+/Li0 (Figure S1a,b). This was equally visible in the SEM micrographs of the current collector (Figure S13c,d) and the cycled graphite electrodes (Figure S14c,d), in which no degradation of the Al or the active materials could be seen. In fact, it appeared that most surfaces in contact with LiPF6− containing electrolytes were covered with decomposition products. EDS imaging of cycled electrodes (Figures S16 and S17) indicated that this deposit was rich in F and P coming from the anion decomposition, as well as O, which could originate from the carbonate solvents. Even though such a layer could protect the electrolyte from decomposition, it could also imply a higher resistance against anion conduction. This was observed in the CV of 1 M LiPF6 in EC/DEC (Figure 1a), which exhibited multiple peaks upon discharge, corresponding to at least 6 distinct staging steps. However, the staging behavior upon charge exhibited a less well-defined appearance in the CV, meaning that the oxidation peaks were not well-separated. This indicated that the intercalation kinetics for PF6− were more sluggish compared to the deintercalation step. In addition, the intercalation of PF6− was particularly difficult to observe during the course of the first cycle, since it was partially masked by the background current due to solvent decomposition. The background current due to electrolyte decomposition further increased for the 4 M LiPF6 electrolyte (Figure 1b), indicating that the PF6− anion triggered side reactions. The electrolyte decomposition did not appear to cease in the course of the first 10 cycles, making the LiPF6 in EC/DEC electrolytes unsuitable for practical applications.

Other essential performance descriptors which define the suitability of a given electrolyte and electrode in DIBs include the specific capacity, Coulombic efficiency (CE) and long-term cycling capability. Galvanostatic experiments conducted in half-cells using both dilute and concentrated electrolytes further indicated that the anions performed differently (Figure 2). The PF6− anion had poor performance in terms of both discharge capacity and CE. In 1 M LiPF6, the CE reached 60%, where it remained during prolonged cycling. The initial discharge capacity was 46 mAh g−1 which decreased to 31 mAh g−1 over 45 cycles (Figures 2e,f and S3). In the 4 M LiPF6 electrolyte, the CE decreased from 60 to 20% over 40 cycles, while the discharge capacity stayed approximately constant at 55 mAh g−1 (Figure 2e,f). A drastic increase in polarization was observed in both electrolytes after the first cycle that was possibly due to the formation of SEI/CEI layers. These observations were again indicative of irreversible surface reactions and anion intercalation. In contrast, an initial discharge capacity of 86 mAh g−1 was obtained in the 4 M LiFSI in EC/DEC. The initial CE was ~50% and increased to 90% in the subsequent cycles. A similar discharge capacity was observed in the 1 M LiFSI in Pyr14FSI electrolyte (84 mAh g−1), but the CE remained low (~60–70%) throughout cycling. This could be partially due to insufficient surface passivation of the lithium negative electrode in the absence of the EC/DEC solvent mixture. However, the previously discussed evidence from SEM/EDS imaging and from the literature indicated that the 1 M LiFSI in Pyr14FSI electrolyte could not passivate the Al current collector to the same extent as the other electrolytes tested. Additional electrochemical experiments conducted to ensure the reliability of the Li reference electrode (Figures S7 and S8) and to investigate the origin of the poor CE (Figure S9) pinpointed parasitic reactions on the graphite cathode as the major problem. Here, it must also be repeated that galvanostatic tests for the 4 M LiFSI in EC/DEC electrolyte were restricted within the potential range of 3.0–4.95 V vs Li+/Li0 (compared to all other electrolytes which were cycled to 5.1 V vs Li+/Li0). The reason for the different cutoff was that an extensive decomposition plateau was observed above 4.95 V vs Li+/Li0 (see Figure S4) for the 4 M LiFSI in EC/DEC electrolyte. The 4 M LiTFSI system exhibited the highest initial discharge capacity (102 mAh g−1) and CE (73%). In the subsequent cycles, the CE increased to 95% as the result of the excellent stability of the TFSI anion and its reversible intercalation in graphite. Further processing of the galvanostatic long-term cycling data (Figures S5 and S6) revealed that the TFSI anion exhibited a highly stable average charge and discharge voltage, as well as the smallest voltage hysteresis among the tested electrolytes. Last, preliminary experiments using a constant-current, constant-voltage (CCCV) protocol (Figures S10 and S11) indicated that there is room for additional performance enhancement, which proved to be especially true for the HCEs based on LiFSI and LiTFSI. In these electrolytes, the introduction of a constant voltage step at the end of discharge led to a significant increase in recovered discharge capacity. Hence, the CE may be further improved by giving the trapped anions additional time to deintercalate.

A detailed XPS study is presented in the following section to better understand the origin of performance differences and the chemical nature of the CEI in the electrolytes investigated so far.
3.2. CEI Probed by X-ray Photoelectron Spectroscopy. 3.2.1. Surface Analysis of Anion-Intercalated Highly Oriented Pyrolytic Graphite. XPS was performed on monolithic, highly oriented pyrolytic graphite (HOPG) electrodes with 1 M LiFSI in Pyr14FSI as the electrolyte for identification of binding energy positions for intercalated anions and anions in electrolyte residues on the surface. The topmost surface of cycled HOPG that was in direct contact with the electrolyte was cleaved to get rid of decomposition residues, thereby exposing a fresh surface for analysis. With such an experimental design, the photoelectron signals originated largely from the intercalated graphite. The XPS study on HOPG electrodes at different states-of-charge is summarized in Figure 3.

The basal plane of HOPG primarily showed a sharp peak (a fwhm of 0.73 eV) due to sp²-hybridized carbons, located around 284.0 eV in the C 1s spectrum. Other, much less intense peaks assigned to sp²-hybridized carbon from adventitious carbon and edge terminations (285.0 eV) and plasmon features (~290.0 eV) could also be observed. After soaking in the electrolyte, the pristine HOPG exhibited more pronounced secondary carbon features originating from −CH₂− groups (285 eV) and the −C−N(+)= bonds (~286.0 eV) of the 1-butyl-1-methylpyrrolidinium (Pyr14⁺) in the ionic liquid. Integration of the areas under the peaks resulted in a 57:43 ratio of −CH₂− and −C−N(+)= bonds, which was in good agreement with the 55:45 ratio calculated from stoichiometric considerations. As expected for Pyr14-FSI, two different nitrogen species were observed in the N 1s spectrum of the ionic liquid: one from the Pyr14⁺ ring located around 401.8 eV and another due to the imide in the FSI anion at 399.1 eV. The intensity of the C 1s peaks from Pyr14⁺ correlated well with the intensity of the N 1s peak at 401.8 eV. After correcting for the atomic sensitivity, the C 1s peaks made up 92% of the total integrated area, while the N 1s peak amounted to 8%, which was very close to the 9:1 ratio expected for carbon and nitrogen in Pyr14⁺ ring. As the only source of sulfur and fluorine atoms, the FSI anion showed a doublet in the S 2p spectrum, located around 169.2 eV due to the sulfonyl moiety, and one main peak with an impurity feature around 687.2 eV due to the fluorine bonded to sulfur. The impact of anion intercalation on the graphite and anion can be observed in the XPS analyses performed on the HOPG electrodes stopped at full charge and discharge conditions.

Figure 3. Investigating the surface composition and evolution of HOPG electrodes: (a) normalized S 2p, F 1s, N 1s, O 1s, and C 1s core-level X-ray photoelectron spectra of pristine, soaked, fully charged (5.1 V vs Li+/Li⁰), and fully discharged (3.0 V vs Li+/Li⁰) HOPG samples. (b) Relative atomic percentages of each chemical species present on the surface of HOPG samples in (a).
Upon charging to 5.1 V vs Li+/Li0, additional peaks emerged in all the spectra and shifts in binding energies were observed. The spectra of the cycled samples were energy-calibrated by aligning the N 1s peak from the FSI anion in nongrounded, surface salt residues to that of the sample at OCV (at 399.1 eV). With this calibration, the main graphite peak shifted to ~284.8 eV, an upshift of 0.8 eV as compared to pristine HOPG. Most importantly, a new peak emerged around 286.0 eV which could likely suggest the formation of (FSI)xC6 intercalation compound in which the anion nitrogen strongly interacts with the graphite framework. Furthermore, the anion intercalation led to significant peak shifts in the N 1s, F 1s, O 1s, and S 2p spectra shown in Figure 3a.

The peak shifts indicated the presence of FSI in two distinct chemical environments. The low BE peaks are thought to correspond to surface-adsorbed FSI anions and the high BE peaks to intercalated, bulk anions. As expected in such a scenario, larger shifts were observed in the nitrogen peak positions compared to the rest of the elements. A 2.91 eV difference between the N 1s peaks from the adsorbed and the intercalated FSI molecules, as opposed to a shift of only 1.41 eV for S 2p and F 1s, suggested that the imide nitrogen interacted more strongly with the graphite framework. This was likely due to the fact that the imide nitrogen could readily donate electrons to the oxidized π-bonding orbitals of graphite. These assumptions were further supported by XPS analyses of Al current collectors cycled in 4 M LiTFSI in EC/DEC and 4 M LiTFSI in EC/DEC electrolytes. No new peaks were observed (see Figures S30 and S31), indicating that the additional peaks did not arise from anion decomposition, but were rather intrinsic of the anion-intercalated HOPG. After discharge to 3.0 V vs Li+/Li0 (FSI deintercalation), the peaks assigned to the intercalated FSI species (N 1s: 401.4 eV, S 2p: 169.8 eV, and F 1s: 687.8 eV) slightly decreased in intensity. A similar effect was observed for the graphite peak assigned to the (FSI)xC6 phase at 286.0 eV. The facts that these peaks persisted even at the discharged state and that the CE was only 38% (Figure S28) proved that the anions could not be fully removed from HOPG in the used voltage range, as reported in previous studies.40−42 These key findings from the HOPG study provided essential reference data for the XPS investigation of composite graphite electrodes presented in the following section.

3.2.2. CEI in Composite Graphite Electrodes. The composite graphite electrodes commonly used in dual-ion batteries consist of carbon black additives and binders. Such electrodes were electrochemically cycled to track changes in the spectra of the graphite active material in the course of anion intercalation and removal for cycles 1, 2, and 10. The formation and chemical nature of the CEI in different electrolytes were investigated by analyzing the C 1s, F 1s, N 1s, O 1s, P 2p, and S 2p spectra.

3.2.2.1. 4 M LiTFSI in EC/DEC. The most intense peak in the pristine C 1s spectra (Figure 4) was attributed to sp2-hybridized carbons in graphite (284.0 eV), while the −CH2− (284.6 eV), −C−O−C− (286.0 eV), and −O−C==O (288.0 eV)
eV) peaks originated from the carbon black additive and CMC binder. In the soaked and cycled electrodes, additional peaks appeared at \( \sim 292.3 \) eV due to the \(-\text{CF}_3\) group of the TFSI anion.

In the C 1s spectrum, the peak around \( \sim 286.0 \) eV increased considerably in intensity as a result of anion intercalation in graphite electrodes charged to 5.1 V. As observed in the HOPG study as well, the \( \text{sp}^2\)-carbon peak shifted to 284.7 eV, and a new peak correlated to the formation of C–N bonds emerged around 286 eV. Similar changes were observed in the spectra of the electrodes charged during cycles 1, 2, and 10. No other new peaks were observed, in contrast to the solid electrolyte interphase (SEI) layer formed on negative graphite electrodes in lithium-ion batteries (LIB) in which both organic and inorganic carbonates are formed due to electrolyte decomposition. The spectra of the electrodes discharged to 3.0 V to remove intercalated anions bore a close similarity to the pristine and soaked electrodes. The intensity of the peak around 286 eV diminished significantly, as the anions were deintercalated from graphite. This confirmed the high reversibility of anion intercalation in the KS6 graphite particles and the fact that the peak was indicative of the strong anion–graphite interaction in the formed intercalation compound. More importantly, both the survey (Figure S39) and C 1s core-level spectra (Figure 4) showed that the \( \text{sp}^2\)-carbon peak of graphite remained the most intense during cycling, which indicated that no substantial electrode–electrolyte interphase layer formed on the graphite particles even after 10 cycles. This could also account for the fact that intercalated anions in the graphite bulk were detected during XPS analyses. Though the absence of a thick interphase could favor the intercalation kinetics, the CE remained lower than 97% over extended cycling (Figure 2f).

Similar to what was observed for HOPG electrodes, the S 2p, F 1s and N 1s spectra split into two sets of peaks upon anion intercalation at 5.1 V (Figure 4). In the S 2p spectra, the S 2p\(_{3/2}\) and S 2p\(_{1/2}\) doublet of the low BE peak appeared at 168.43 and 169.59 eV (±0.30 eV). The doublets of the high BE peak were located around 169.68 and 170.84 eV (±0.25 eV). The peak-to-peak difference between the S 2p\(_{3/2}\) components of the two doublets was 1.25 ± 0.11 eV. As pointed out above, the additional peaks indicated the formation of rather localized C–N bonds in the graphite intercalation compound. As expected, the peak shift in the F 1s spectra was relatively smaller (0.87 ± 0.02 eV), with the low and high BE peaks located at 688.27 ± 0.11 eV and 689.14 ± 0.10 eV, respectively. The fluorine atoms in the \(-\text{CF}_3\) group were affected less by the oxidizing nature of the anion-intercalated graphite. The formation of the intercalation compound was highly reversible, as the peaks belonging to intercalated TFSI (at higher BEs) nearly disappeared upon

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**Figure 5.** Surface analyses of pristine, soaked and cycled graphite electrodes: The C 1s, S 2p, F 1s, and N 1s core level spectra of positive graphite electrodes cycled in 4 M LiFSI in EC/DEC were used to study the formation and stability of the CEI during cycles 1, 2, and 10. The electrodes were charged to 4.95 V vs Li+/Li\(^0\) and discharged to 3.0 V vs Li+/Li\(^0\) prior to XPS study.
The residual intensity corresponds to a certain amount of anions remaining trapped, either within the graphite bulk or bonded to the edge defects.

3.2.2.2. 4 M LiFSI in EC/DEC. XPS surface analyses of the composite electrodes cycled in 4 M LiFSI in EC/DEC exhibited interface characteristics essentially similar to those of the electrodes in 4 M LiTFSI in EC/DEC electrolyte (Figures 5 and S37). FSI intercalation and deintercalation was confirmed by the intensity changes of the C 1s peak at ∼286.0 eV, as well as emergence of new peaks in the S 2p, F 1s, and N 1s peaks at higher BE. In the S 2p spectra, a pair of doublets appeared at 169.20 eV (2p3/2) for the low BE peak and at 170.50 eV (2p3/2) for the high BE peak, which resulted in an average energy difference of 1.29 ± 0.13 eV. With regard to the N 1s spectra, the low BE peak was set to 399.20 eV, while the high BE peak appeared at 401.52 ± 0.26 eV, leading to a separation of 2.32 ± 0.26 eV difference. Removal of the anions during discharge to 3.0 V resulted in the disappearance of the new peaks and in the graphite C 1s peak shifting to lower BE. These observations held true for all electrodes after cycles 1, 2, and 10, and conclusively demonstrated that the intercalation process was reversible even though no permanent CEI layer formed on the electrodes. The absence of a stable passivation layer at the interface was manifested in the poor CE of FSI anion cycling in graphite, which was approximately 90% over 50 cycles as shown in Figure 2f.

3.2.2.3. 1 M LiFSI in Pyr14FSI. The electrodes cycled in the ionic liquid electrolyte showed similar XPS characteristics (Figure 6) to those electrodes cycled in the concentrated sulfonimide electrolytes. In the S 2p spectra, the low BE doublet appeared at 169.13 eV (2p3/2) and the high BE doublet at 170.40 eV (2p3/2), leading to a difference of 1.28 ± 0.17 eV. As observed for the FSI-intercalated graphite electrodes in 4 M LiFSI in EC/DEC, two peaks were detected in the F 1s spectra, around 686.87 ± 0.44 eV and 688.33 ± 0.44 eV, leading to a separation of 1.46 ± 0.23 eV. The energy separation between the F 1s peaks suggested that the anions interact differently with graphite, as this was much smaller for TFSI (0.87 ± 0.02 eV). In addition, it should be noted that the high BE peak assigned to F in the intercalated species did not seem to decrease in intensity relative to the nonintercalated species upon discharge, which could in addition be indicative of the partial breakdown of the S–F bond at high operating voltages. However, the exact nature of the excess fluorine detected has not been identified here. As discussed above, BE difference between the two peaks in the N 1s spectra was 2.61 ± 0.16 eV (peaks at 399.10 eV and 401.71 ± 0.16 eV), whereas no intensity decrease was observed in the high BE peaks upon discharge. Both of these phenomena could be
attributed to surface residues of the \( \text{Pyr}_{14}^+ \) cation, which has a positively charged nitrogen with a BE around 402.5 eV.

Ideally, similar changes and trends (as in the N 1s, S 2p, and F 1s spectra) should be expected in the O 1s spectra (for all of the electrolytes based on sulfonimide anions), as confirmed by XPS analyses on the HOPG electrodes. Nonetheless, in the case of the composite electrodes, there were several other oxygen-containing species (solvent, binder, and conducting additive), which would complicate the spectral interpretation. The O 1s spectra are provided as Figure S33. Finally, the Li 1s spectra for these electrolytes are also provided in Figure S32, where it is shown that principally no Li was detected on the surface of the graphite electrodes.

3.2.2.4. 1 M and 4 M LiPF\(_6\) in EC/DEC. As discussed earlier and shown in the SEM images (Figure S14), the graphite particles cycled in both 1 and 4 M LiPF\(_6\) electrolytes had a thick layer of decomposition products on the surface. In contrast to the sulfimide electrolytes, a CEI layer was formed during cycling. In the spectra of the soaked electrodes, peaks assigned to \(-\text{CH}_2\)− (284.8 eV), \(-\text{C}-\text{O}-\text{C}-\) (286.0 eV), and \(-\text{O}--\text{C}==\text{O}\) (287.0−288.0 eV) functional groups were observed. Furthermore, a less intense signal was detected at a binding energy of 289.0−290.0 eV corresponding to \(-\text{O}--\text{CO}_2\)− groups. Upon charging, the peaks increased in intensity due to accumulation of polyethers, and polycarbonates originating from the oxidative decomposition of EC. Although theoretical studies recognize EC as being relatively inert toward oxidative degradation (up to 5.5 V vs Li\(^+/\text{Li}^0\)), its stability can be altered significantly in the presence fluorinated anions.\(^{45}\) The decomposition of EC on the negative electrode usually involves ring opening and dimerization leading to the formation of diverse alkyl carbonates, e.g., \((\text{CH}_2\text{OCO}_2\text{Li})_2\).

The generation of similar reaction products on the positive electrode is highly probable and has been observed for transition metal oxide cathodes operating above 4.0 V vs Li\(^+/\text{Li}^0\).\(^{46}\) Here, it appears as if the higher salt concentration has, instead of leading to improved electrolyte stability, induced further decomposition.

Apart from EC, the salt gave rise to additional decomposition products as confirmed in the survey (Figures S40 and S41) and in the F 1s spectra of the LiPF\(_6\) systems (Figure 7). The F 1s peak was particularly intense, suggesting that the CEI is rich in fluorine-containing compounds, possibly LiF, LiPF\(_x\), and PO\(_x\)F\(_y\) (\(x \leq 5\)). Further evidence for the existence of these species can be seen in the Li 1s (Figure S34) and P 2p (Figure S35) spectra. The presence of Li in the CEI was confirmed by a broad peak at 57.5 eV. The maximum of the P 2p doublet appears at approximately 136.3 eV for the OCV sample, which is in good agreement with the literature value for phosphorus in PF\(_6\)− and PF\(_x\)F\(_y\) (\(x \leq 5\)). After anion cycling in the graphite electrodes, the P 2p peak at the lower BE (~135.0 eV) increased in intensity, which is in agreement with the increase in the PO\(_x\)F\(_y\) species.

Notably, in the case of LiPF\(_6\)-based electrolytes, the peaks due to anion intercalation could not be observed clearly in any of the spectra as a result of the high amount of decomposition products covering the electrode surface. As mentioned earlier, electrolytes based on LiPF\(_6\) have shown the ability to form solid electrolyte interphases rich in inorganic compounds such as LiF, LiPF\(_x\), and LiPF\(_x\)O\(_y\), as well as organic decomposition products, owing to the partial hydrolysis of the PF\(_6\)− anion. The exact physicochemical properties of these interphases could vary substantially, depending on the electrode material, electrolyte formulation and cycling conditions.\(^{47}\) Here, severe

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**Figure 7.** Nature and evolution of the electrode–electrolyte interface on positive graphite electrodes during cycles 1, 2, and 10. The spectra of the pristine, soaked, and cycled graphite electrodes are shown. The cycled electrodes were charged to 5.1 V vs Li\(^+/\text{Li}^0\) and discharged to 3.0 V vs Li\(^+/\text{Li}^0\) prior to XPS study. The C 1s and F 1s core level spectra of positive graphite electrodes cycled in 1 M LiPF\(_6\) in EC/DEC (a) and in 4 M LiPF\(_6\) in EC/DEC (b) indicated the formation of surface film composed of decomposition products from the electrolyte.
Electrolyte decomposition was observed over 50 cycles, resulting in a thick CEI layer and demonstrating that electrolytes combining LiPF_6 (as the main salt) and EC might be unsuitable for use in GDIBs.\textsuperscript{37}

The XPS findings described in this section correlated well with both electrochemical and microscopy characterizations. To summarize, three ideal cases can be envisaged regarding the nature and stability the CEI, as shown schematically in Figure 8d. In concentrated sulfonimide salt electrolytes, no substantial CEI, apart from a thin layer of chemisorbed anions, was formed on graphite particles even after 10 cycles. Apart from XPS and SEM, these observations were verified through TEM characterization (Figures 8a–c and S20–S23). The TEM images confirmed that no CEI resided on the graphite particles cycled in the LiFSI/LiTFSI-based HCEs and IL, as the graphite lattice fringes continue until the edge of the KS6 particles. (d) Schematic illustration of a graphite particle without CEI (1), with a blocking CEI (2), and with a CEI permeable to the anion intercalant (3). The third case is the most desirable, as this functional CEI allows for the insertion/deinsertion of the anion, while it blocks the solvent molecules from entering the graphite, causing side reactions and aggravated exfoliation.

The XPS analysis highlighted the presence of a thin CEI layer composed of adsorbed anions, through which the intercalated species could be simultaneously probed. The signals of intercalated anions appeared to shift toward higher binding energies relative to the adsorbed species. The shift was element-dependent, with N 1s showing the largest shift (2.9 vs 1.4 eV for S 2p, F 1s, and O 1s), which indicated a stronger interaction between the anion nitrogen and the graphite. In addition, the anion-intercalated graphite gave rise to a distinct peak, shifted $\sim$0.7 eV to the main C 1s line. XPS performed on composite graphite electrodes cycled in 4 M LiFSI/LiTFSI in EC/DEC and in 1 M LiFSI-IL indicated the formation of a similar interface to that of HOPG. The absence of a conventional CEI proved that these systems are kinetically stabilized, owing to the high salt concentration. Systems cycled in LiPF_6-containing electrolytes resulted instead in a thicker CEI, rich in EC-derivatives (polyethers and polycarbonates) and decomposed salt (Li_xPF_6/PO_4_{3-x}/LiPO_{4-x}). Extensive breakdown occurred irrespective of the LiPF_6 concentration, which indicated that these electrolyte compositions are unsuitable for GDIBs. Nonetheless, the passivating layers observed on both the Al current collector and graphite electrode highlighted the potential of LiPF_6 as a CEI-forming additive. Using LiPF_6 alongside other CEI-forming additives in concentrated sulfonimide electrolytes is the subject of an ongoing study, targeting a further increase in the stability of electrolytes tailored for graphite dual-ion batteries.

4. CONCLUSIONS

The highly concentrated electrolytes (4 M) based on LiFSI/LiTFSI in EC/DEC delivered a superior electrochemical performance compared to the other systems studied, in terms of anion intercalation kinetics, specific discharge capacity (86 mAh g\textsuperscript{-1} for LiFSI and 102 mAh g\textsuperscript{-1} for LiTFSI) and CE (90–95\% after 10 cycles). The 4 M LiTFSI in EC/DEC electrolyte proved stable up to 5.1 V vs Li/Li\textsuperscript{0}, while 4 M LiFSI in EC/DEC was limited to 4.95 V vs Li/Li\textsuperscript{0}. A high salt concentration (≥4 M) proved essential in order to stabilize the Al current collector and enable electrochemical cycling. The IL electrolyte (1 M LiFSI in Pyr14FSI) exhibited a similar electrochemical stability window (5.1 V vs Li/Li\textsuperscript{0}) and specific discharge capacity (84 mAh g\textsuperscript{-1}). However, the IL suffered from inferior kinetics of anion intercalation and poor CE (~60–70\%). Electrolyte systems based on LiPF_6 salt (at 1 and 4 M concentrations) resulted in low discharge capacities (~46–55 mAh g\textsuperscript{-1}), high intercalation overpotentials, and substantial irreversibility (CE: 20–60\%), linked to the decomposition of the PF_6\textsuperscript{-} anion and ethylene carbonate solvent.

The electrochemistry was supported by post-mortem XPS measurements. XPS performed on HOPG cycled in 1 M LiFSI in Pyr14FSI revealed the presence of a thin CEI layer composed of adsorbed anions, through which the intercalated species could be simultaneously probed. The signals of intercalated anions appeared to shift toward higher binding energies relative to the adsorbed species. The shift was element-dependent, with N 1s showing the largest shift (2.9 vs 1.4 eV for S 2p, F 1s, and O 1s), which indicated a stronger interaction between the anion nitrogen and the graphite. In addition, the anion-intercalated graphite gave rise to a distinct peak, shifted $\sim$0.7 eV to the main C 1s line. XPS performed on composite graphite electrodes cycled in 4 M LiFSI/LiTFSI in EC/DEC and in 1 M LiFSI-IL indicated the formation of a similar interface to that of HOPG. The absence of a conventional CEI proved that these systems are kinetically stabilized, owing to the high salt concentration. Systems cycled in LiPF_6-containing electrolytes resulted instead in a thicker CEI, rich in EC-derivatives (polyethers and polycarbonates) and decomposed salt (Li_xPF_6/PO_4_{3-x}/LiPO_{4-x}). Extensive breakdown occurred irrespective of the LiPF_6 concentration, which indicated that these electrolyte compositions are unsuitable for GDIBs. Nonetheless, the passivating layers observed on both the Al current collector and graphite electrode highlighted the potential of LiPF_6 as a CEI-forming additive. Using LiPF_6 alongside other CEI-forming additives in concentrated sulfonimide electrolytes is the subject of an ongoing study, targeting a further increase in the stability of electrolytes tailored for graphite dual-ion batteries.
Further electrochemical characterization of Al current collectors and graphite cathodes, SEM and EDS of cycled Al current collectors and KS6 graphite cathodes, ex situ TEM of cycled graphite cathodes, Raman spectroscopy of pristine cycled graphite cathodes, XRD of pristine cycled graphite cathodes, complementary XPS data on cycled, highly ordered pyrolytic graphite and KS6 graphite (PDF).

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**Author Contributions**

A.K. and H.D.A. designed the project and wrote the first draft of the manuscript. A.K. performed the SEM characterizations, electrochemical testing and XPS measurements and processed the data. H.D.A. contributed to the analysis and interpretation of the electrochemical data. C.W.T. performed the TEM characterization. M.H. and K.E. participated in the design and characterization of the electrochemical data. All authors contributed to the discussions of the results and the revision of the original draft of the manuscript.

**Notes**

The authors declare no competing financial interest.

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