



Article

Regeneration of Spent Graphite from Lithium-Ion Batteries by Malic-Acid Leaching and Alkaline EDTA Chelation

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Abstract

The electrochemical reuse of spent graphite from the negative electrodes of lithium-ion batteries is influenced by regeneration-induced changes in near-surface chemical and defect states. These states govern solid electrolyte interphase (SEI) re-formation, particularly when bulk contaminants are suppressed. Acidic malic-acid leaching and ethylenediaminetetraacetic acid chelation under alkaline conditions (pH 8.7) were compared under similar operating parameters to isolate the role of the leaching environment. This was followed by heat treatment at 1200 °C to decouple chemical cleaning from structural restoration. Both methods reduced the total impurities from 217.85 ppm to ~1.8 ppm, approaching that of commercial graphite. Despite the comparable bulk purity, depth-resolved X-ray photoelectron spectroscopy after formation cycling revealed distinct outermost surface states relevant to SEI re-formation: acidic processing yielded a more oxygenated carbon signature and higher LiOH fraction at the outermost surface (~16%), whereas alkaline chelation produced a more graphitic, carbonate-dominated surface with lower LiOH (~7%). Electrochemical and impedance measurements were consistent with these differences, suggesting that after the bulk impurities were minimized, resistance development was largely governed by the leaching-conditioned near-surface state, which biased the SEI composition. The comparison under matched conditions linked the regeneration environment to SEI-relevant surface speciation and provided a mechanistic basis for selecting regeneration routes to reuse spent graphite as a negative-electrode active material.

Keywords: spent graphite; lithium-ion battery recycling; graphite regeneration; organic acid leaching; ethylenediaminetetraacetic acid chelation; heat treatment; solid electrolyte interphase



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1. Introduction

Lithium-ion batteries (LIBs) are widely used in electric vehicles and stationary energy-storage systems. As production increases, manufacturing scrap and end-of-life cells are being generated in growing quantities, increasing the importance of efficient recycling [1,2]. Most industrial-recycling routes prioritize positive-electrode materials because of their metallic value. In contrast, negative electrodes (mainly graphite in commercial LIBs) often receive less attention, despite constituting a large fraction of the cell mass [3,4]. Recovered

graphite is frequently downcycled or discarded because purification is challenging, and its electrochemical performance after processing remains uncertain [4,5]. Moreover, life-cycle assessments suggest that the environmental footprint of graphite recycling and upgrading is sensitive to electricity demand and chemical inputs, particularly acids [5]. Therefore, regeneration strategies are required to enable the reuse of recovered graphite as a negative-electrode active material in new LIBs.

This challenge arises because recovered graphite can differ substantially from pristine battery graphite in terms of chemistry and structure. Spent negative-electrode materials can contain Li-bearing residues (e.g., LiF and Li₂CO₃) and remnants of binder and conductive additives [6–8]. They can also carry surface films formed by electrolyte decomposition, commonly referred to as the solid electrolyte interphase (SEI) [6–8]. Metallic impurities may also remain, including copper particles and, in some cases, transition-metal species originating from the positive electrode [4,5]. In addition, electrochemical aging and mechanical handling during dismantling can increase defect density and disturb the graphite stacking order [4,5,9,10]. These changes directly affect reuse. Residues and defect-rich regions can alter SEI re-formation, increase interfacial resistance, and accelerate impedance growth, thereby decreasing the initial Coulombic efficiency and degrading cycling stability [6–8]. Therefore, effective regeneration requires impurity removal while minimizing damage to the graphite framework and preconditioning the near-surface state that governs SEI re-formation.

A range of approaches for regenerating spent graphite has been investigated. Washing and physical separation can remove residual electrolytes and some polymeric species; however, Li salts and metal contaminants may persist in the near-surface regions or within agglomerates [4,5]. Mineral-acid treatments, for example, sulfuric-acid curing/leaching followed by high-temperature calcination, can improve the graphite purity [11]. However, acid-based processes impose corrosion and wastewater-treatment requirements and may alter graphite surfaces through oxidation and defect formation [4,11,12]. Thermal routes can decompose organic residues and may improve crystallinity, while ultrafast Joule heating (“flash”) has been proposed as a rapid option [13,14]. However, thermal approaches encounter practical constraints related to energy input, equipment, and the incomplete removal of inorganic salts or metals [4,13,14]. These reports suggest that high-impurity removal alone does not ensure electrochemical recovery. Moreover, the surface and defect states created during processing remain as limitations.

Among the wet-chemical options, organic acids have been explored as milder leachants than strong mineral acids because carboxylate-containing molecules provide acidity and metal-binding abilities [4]. Citric-acid leaching enables the recovery and reuse of graphite with competitive performance when combined with suitable downstream processing [15]. Water-based treatments have also been proposed as lower-hazard routes [16]. However, many organic-acid methods operate at low pH, generating substantial salt streams and requiring extensive washing and neutralization. Low-pH exposure can also modify the surface functional groups and defect populations, which can later influence the SEI chemistry and interfacial-resistance evolution [4,6–8]. These limitations motivate comparisons with chemistries that depend less on proton-driven dissolution.

Chelation-based leaching in neutral-to-alkaline media offers an alternative route in which impurities are mobilized primarily through complexation. Ethylenediaminetetraacetic acid (EDTA) forms stable aqueous complexes with many metal ions; therefore, it can promote the extraction of metal impurities without relying on strong acidity [17]. EDTA-based leaching has been used to achieve a high overall elemental recovery from spent LIB materials [17], suggesting that alkaline chelation may remove contaminants while reducing acid-driven surface modification. For the regeneration of spent graphite from a

negative electrode, the direct benchmarking of alkaline chelation against acidic organic-acid leaching under comparable operating conditions remains limited [4]. Studies evaluating both approaches using a consistent set of metrics (impurity levels, structural and defect evolution, SEI-relevant surface chemistry, and electrochemical behavior) are also scarce. This gap is important because the leaching environment can influence contaminant extraction and the near-surface state, which controls SEI re-formation and impedance growth [6–8].

This study compares malic-acid leaching under acidic conditions and EDTA chelation under alkaline conditions using matched operating parameters (solid-to-liquid ratio, temperature, and holding time) to isolate the effects of the leaching environment. The reagent concentrations and pH are selected to represent practically relevant acidic and alkaline regimes; malic acid serves as a model dicarboxylic organic acid for the proton-assisted leaching regime, whereas EDTA is used as a benchmark chelating agent for complexation-dominated extraction. A subsequent high-temperature treatment step (1200 °C) is included to decouple chemical cleaning from structural recovery by promoting graphitic ordering and mitigating the defect-associated reactivity [14]. The regenerated materials are then assessed by bulk-impurity quantification, structure- and surface-sensitive characterization, and half-cell testing (capacity, initial Coulombic efficiency, polarization, rate performance, and cycling stability). Depth-resolved X-ray photoelectron spectroscopy (XPS) is used to determine how the regeneration conditions precondition the near-surface region relevant to SEI re-formation. These analyses clarify how acidic and alkaline regeneration environments modify the surface and structure of recovered graphite and provide a practical basis for selecting regeneration chemistries for reuse as negative-electrode active materials.

2. Results and Discussion

2.1. Morphology and Residual Contaminant Distribution in Spent and Regenerated Graphite

Field-emission scanning electron microscopy (FE-SEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental maps (Figure 1a,(a-1)) show that spent graphite (SG) retains deposit-rich surface films with adhered particulates. In the corresponding EDS maps, oxygen, fluorine, and phosphorus signals are broadly detected across the SG surface, with Al localized in particulate-rich regions (Figure 1(a-1)), consistent with mixed electrolyte- and binder-derived residues (P from LiPF₆-derived species and F from electrolyte-derived fluorides and polyvinylidene fluoride (PVDF) fragments) persisting within the deposit layer [18]. Such mixed deposit chemistry provides a plausible basis for spatially nonuniform interphase re-formation. In contrast, the regenerated samples exhibit markedly reduced surface deposits and attenuated heteroatom signals in the EDS maps (Figure 1b,c,(b-1),(c-1)), consistent with detachment of the deposit layer and re-exposure of the underlying graphite basal and edge planes.

Transition-metal signals (e.g., Ni, Co, and Mn) are spatially localized and tend to co-occur with deposited particulates rather than appearing as uniform backgrounds (Figure 1(a-1)). This spatial colocalization suggests that most metallic impurities are present as discrete particulates or surface-attached fragments, rather than being incorporated into the graphite lattice. Such localization may contribute to spatially heterogeneous interphase formation during subsequent cycling [19,20]. The observed distribution is consistent with the positive-electrode-to-negative-electrode crosstalk during long-term cycling and the physical carryover of positive-electrode fragments during dismantling.

After wet chemical regeneration, the malic-acid-treated graphite (MG; obtained via acidic malic-acid leaching) and EDTA-treated graphite (EG; obtained via EDTA chelation under alkaline conditions (pH 8.7)) exhibit reduced surface deposits (Figure 1b,c), with elemental maps dominated by carbon and diminished oxygen-rich features (Figure 1(b-1),(c-1)). This change is consistent with the detachment of the deposit phases and re-exposure of

the underlying graphite basal and edge planes. Because the basal and edge planes differ in surface reactivity and functional-group density, the extent and chemistry of this re-exposed surface are expected to influence the initial pathways of SEI re-formation during formation cycling. The smoother basal texture and sharper edge features become more evident after regeneration, approaching the surface morphology of commercial graphite (CG) (Figure 1d).

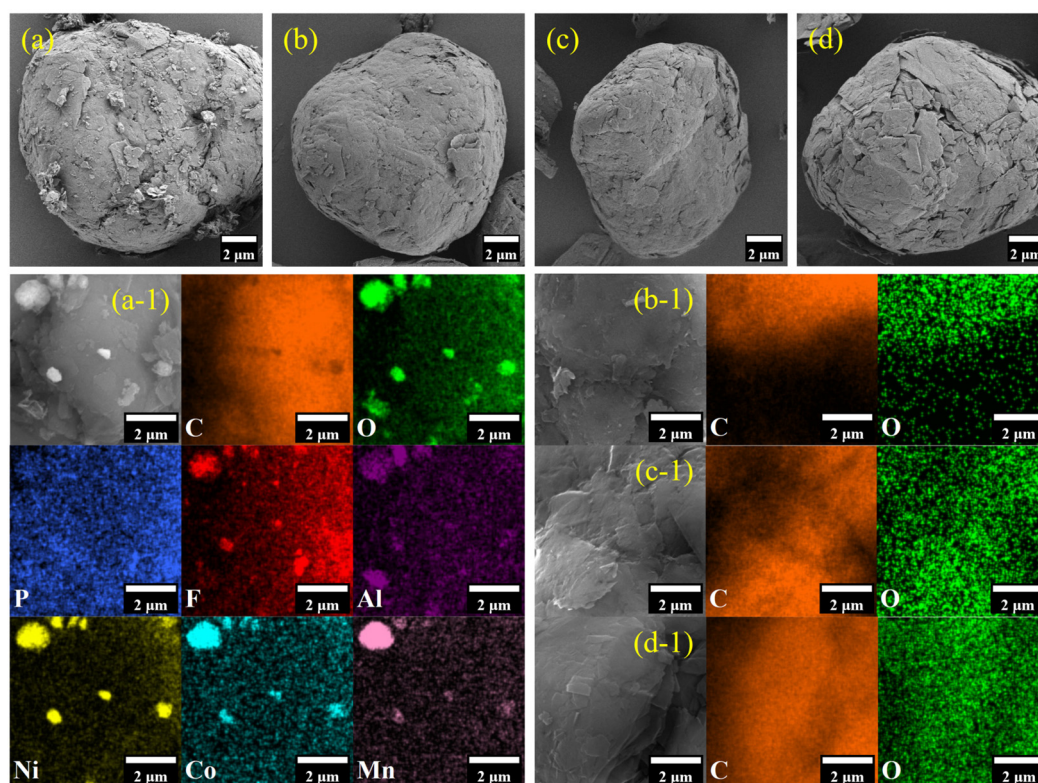


Figure 1. Field-emission scanning electron microscopy (FE-SEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental maps of graphite samples: (a) spent graphite (SG), (b) malic-acid-treated graphite (MG), (c) ethylenediaminetetraacetic acid (EDTA)-treated graphite (EG), and (d) commercial graphite (CG); (a-1) representative EDS maps of SG (C, O, P, F, Al, Ni, Co, Mn); (b-1–d-1) representative C and O maps for MG, EG, and CG.

Consistent with this morphological recovery, the heteroatom (F and P), Al, and transition-metal signals that are prominent or localized in the SG are substantially suppressed in the regenerated samples (often near the EDS-mapping sensitivity). The resulting maps are C-dominated, with only weak O contributions (Figure 1(b-1)–(d-1)). This re-exposure of the basal and edge planes is expected to recover electrochemically accessible graphite surfaces for subsequent lithiation and delithiation. The reduced deposit phases and metal-bearing particulates may decrease the electrochemically inactive surface blockage, thereby limiting the localized sites for parasitic electrolyte decomposition [19,21]. The implications for interfacial resistance are discussed in Section 2.5. These changes indicate the concurrent removal of physically and chemically distinct contaminant phases and alteration of the near-surface chemical state that governs interphase formation and impedance evolution. Next, the extent of impurity removal was quantified by ICP–MS (Section 2.2). The chemical speciation of the residual near-surface layer is discussed later using depth-resolved XPS (Section 2.6).

2.2. Quantitative Impurity Removal by Malic-Acid Leaching and EDTA Chelation

Inductively coupled plasma mass spectrometry (ICP–MS) shows that both malic-acid leaching (performed with glucose as a reducing agent; Section 3.2) and EDTA chelation reduce the elemental impurity levels in SG by >99% under matched conditions (Figure 2a). This brings the total impurity levels close to the commercial benchmark (Figure 2 and Table S1). SG contains a high total-impurity concentration (217.85 ppm; Figure 2b), dominated by Ni (122.02 ppm) with additional contributions from Li, Mn, Co, and Al (Figure 2a). This transition-metal-rich profile is consistent with the positive-electrode-derived species reaching the negative electrode during cycling or via carryover during dismantling (Section 2.1).

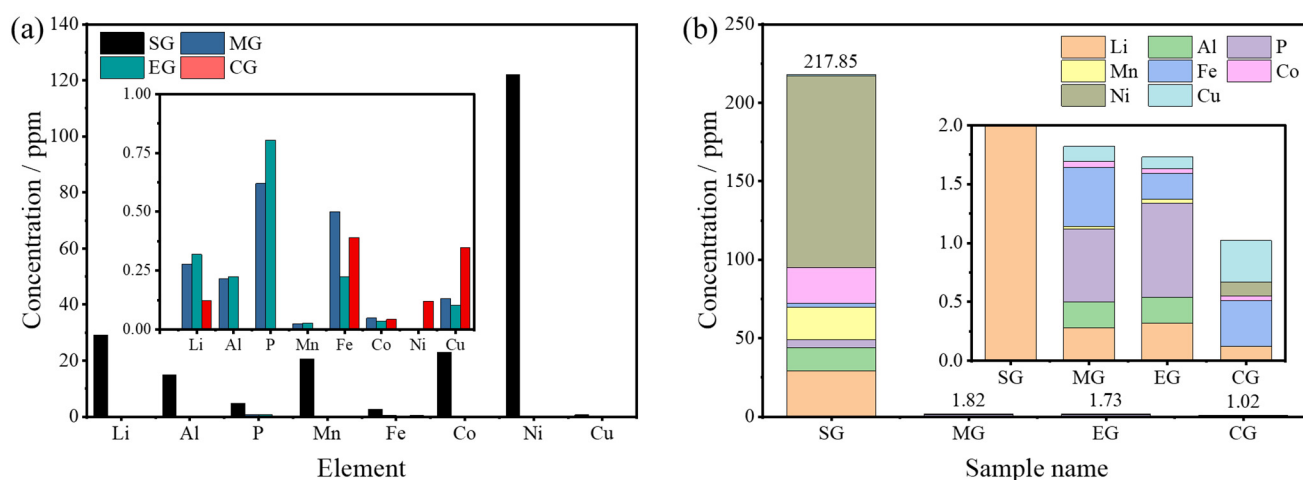


Figure 2. Inductively coupled plasma mass spectrometry (ICP–MS) impurity concentrations in SG, MG, EG, and CG: (a) element-by-element comparison (inset: magnified low-concentration region (parts per million, ppm)); (b) stacked contributions and total impurity levels (inset: magnified view of MG, EG, and CG).

After regeneration, the total impurities decrease close to the commercial benchmark (1.82 ppm for MG and 1.73 ppm for EG, versus 1.02 ppm for CG; Figure 2b), corresponding to a >99% reduction relative to SG. For Ni and Co, concentrations decrease from 122.02 and 22.98 ppm in SG to below the detection limit for Ni and ~0.04–0.05 ppm for Co in MG/EG (Figure 2a, inset), indicating that both approaches reduce transition-metal contaminants to sub-ppm levels. Deposited transition metals can accelerate parasitic electrolyte reactions and destabilize the interphase development [19,21]. Therefore, achieving sub-ppm levels can isolate the route-dependent effects of leaching-induced near-surface chemical and defect states. In this regime, transition-metal-catalyzed parasitic reactions are minimized as dominant variables, and electrochemical recovery becomes more sensitive to the leaching-conditioned surface functional groups and defect populations that govern SEI re-formation.

With the suppression of dominant transition metals, the residual impurity budget becomes more diagnostic of minor sources. In both MG and EG, P- and Fe-containing species accounted for most of the remaining sub-ppm levels (Figure 2a, inset). This pattern is consistent with the electrolyte-salt-derived and hardware-related trace contributions becoming more apparent once the transition metals are removed. Al and Cu detected at low levels may reflect minor current collectors or casing-derived particulates introduced during recovery. The comparable post-treatment impurity levels (Figure 2b) suggest that bulk purification is unlikely to be the main discriminating factor between the two chemistries under the same conditions. Because ICP–MS quantifies the bulk composition after digestion, near-surface residues relevant to SEI formation can differ between routes, even at comparable total-impurity levels. Instead, the remaining differences in

performance may be associated with the interaction of the two leaching environments with the graphite surface during contaminant extraction.

These two regeneration environments mobilize contaminants through distinct chemical driving forces. In the malic-acid approach (pH 2.2), metal oxides/hydroxides dissolve primarily via proton-promoted weakening of M–O bonds, which increases metal-ion solubility [22]. Carboxylate ligands can additionally stabilize the dissolved metals and further shift the dissolution equilibria. In the EDTA route (pH 8.7), extraction proceeds mainly by chelation; stable metal–EDTA complexes lower the activity of dissolved ions and sustain ligand-promoted dissolution under alkaline conditions [23]. EDTA provides multidentate carboxylate and amine donor sites that remain effective at pH 8.7, enabling complexation-driven extraction without strong acidity. Once the total impurities are reduced to ~1–2 ppm by either route (Figure 2b), the remaining differences in the electrochemical recovery are more plausibly governed by the surface and defect states generated during leaching. This leaching-induced state can influence the subsequent SEI re-formation and resistance growth [24,25]. Accordingly, Sections 2.3 and 2.6 focus on route-dependent changes in the sp^2 framework and near-surface speciations that control the interphase evolution.

2.3. Structural Ordering and Defect Evolution After Regeneration and Heat Treatment

X-ray diffraction (XRD) and Raman spectroscopy show that the acidic and alkaline wet-chemical regeneration routes impose different degrees of lattice perturbation and defect evolution (Figure 3). Here, the suffix “-H” denotes the heat-treated counterparts of the wet-regenerated samples (1200 °C post-treatment; Section 3.3), i.e., MG-H and EG-H are obtained by heat treating MG and EG, respectively. To distinguish the respective contributions of wet impurity removal and thermal post-treatment, MG and EG represent the materials after wet processing (before 1200 °C), while MG-H and EG-H represent the corresponding materials after the identical 1200 °C post-treatment (Section 3.3). Accordingly, the wet-processing effect is assessed by SG → MG/EG, and the incremental heat-treatment effect is assessed by MG → MG-H and EG → EG-H. The subsequent heat treatment partially restores graphitic ordering.

In the XRD patterns (Figure 3a), SG shows additional reflections that can be indexed to Ni and NiO alongside the graphite peaks, consistent with the high Ni level measured by ICP–MS. These impurity-related reflections are suppressed after wet processing and are no longer prominent after heat treatment, consistent with either the removal of crystalline Ni/NiO phases or a reduction below the XRD-detection limit. In the enlarged (002) region (Figure 3b), MG shows a slightly broader and lower-angle (002) reflection than EG, suggesting greater interlayer expansion and stacking disorder after acidic leaching. The corresponding d_{002} values are of 3.414 and 3.404 Å for MG and EG, compared with 3.396 and 3.371 Å for SG and CG, respectively. After the heat treatment, the (002) peak sharpens and shifts toward CG. EG-H shows the closest agreement with CG ($d_{002} = 3.371$ Å), whereas MG-H remains slightly expanded ($d_{002} = 3.381$ Å). This residual expansion suggests that some acid-conditioned lattice perturbation persists after thermal treatment. The corresponding near-surface chemical signatures are discussed in Section 2.6. The larger (002) shift and broadening of MG are consistent with stronger lattice perturbations during acidic leaching. This may reflect the acid-promoted generation of oxygenated edge/defect sites (Section 2.6), which may weaken interlayer cohesion. In comparison, the EDTA route (pH 8.7) shows a smaller shift, consistent with limited stacking disruption under the present conditions.

Raman spectra are commonly used to qualitatively assess defect- and edge-related disorders using the D-to-G band area ratio (A_D/A_G) [26,27] (Figure 3c). The D band (~ 1350 cm^{-1}) and G band (~ 1580 cm^{-1}) are used to compute A_D/A_G . The SG exhibits the

highest defect signature ($A_D/A_G = 0.47$). Wet-chemical regeneration decreases A_D/A_G to 0.44 (MG) and 0.38 (EG), consistent with a reduced defect- and edge-related contribution, even before heat treatment. Heat treatment further reduces A_D/A_G to 0.28 and 0.22 for MG-H and EG-H, respectively, with EG-H approaching CG (0.21). The relative magnitude of the A_D/A_G change separates deposit removal from framework recovery. The modest A_D/A_G decrease after wet processing (MG and EG), relative to the pronounced decrease after heat treatment, indicates that deposit removal and impurity extraction alone do not fully restore the sp^2 framework. Therefore, substantial defect healing and restacking require high-temperature treatments. A_D/A_G reflects both intrinsic structural disorder and contributions from edge-rich/disordered surface deposits; accordingly, the decrease after wet processing is attributed to deposit removal, together with the partial recovery of the underlying graphitic framework.

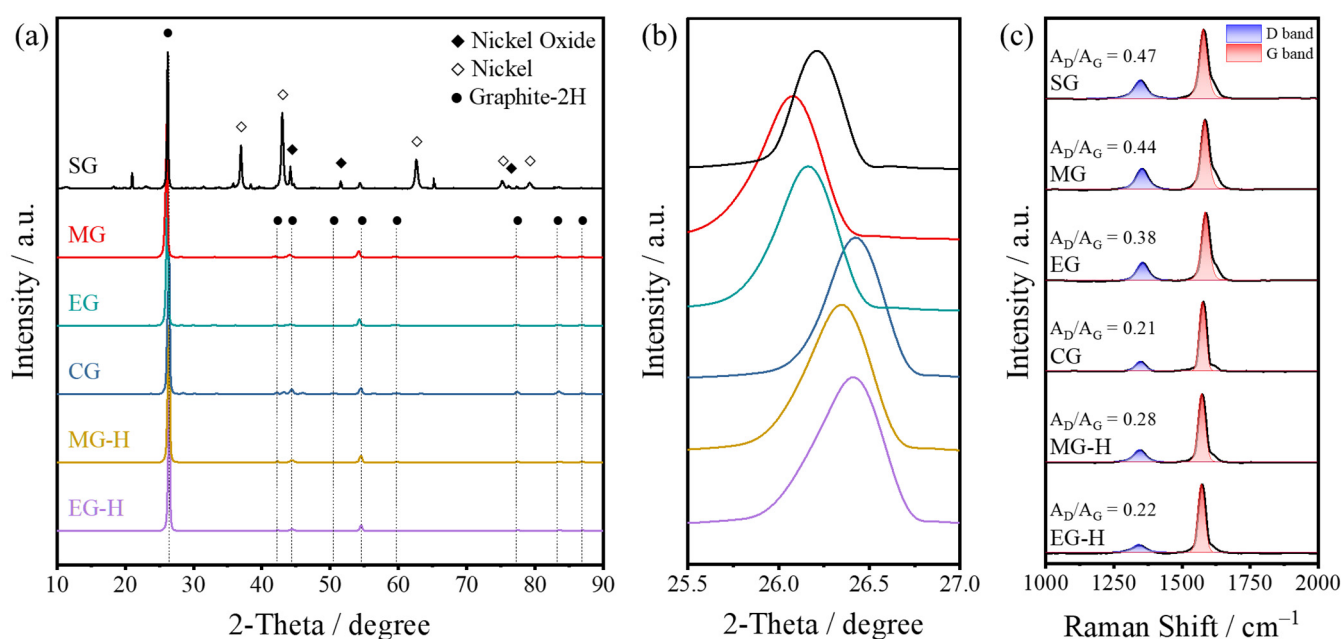


Figure 3. Structural characterization of regenerated graphite: (a) X-ray diffraction (XRD) patterns (Ni/NiO reflections marked); (b) enlarged graphite (002) region; (c) Raman spectra, and A_D/A_G (D-band area to G-band area ratio) for SG, MG, EG, CG, MG-H, and EG-H. MG-H and EG-H denote MG and EG after the 1200 °C heat-treatment step (Section 3.3).

Consistent with the (002) behavior (Figure 3b), the alkaline route (from EG to EG-H) achieves a lower residual disorder after heat treatment (Figure 3c), suggesting that minimizing the chemical perturbation during wet processing facilitates a more complete structural recovery upon heat treatment. This trend suggests that acidic leaching may introduce or preserve more defect/edge-reactive sites than alkaline chelation, whereas the high-temperature treatment promotes defect healing, restacking, and the removal of defect-associated surface functionalities [28–31]. Therefore, the structural data suggest that regeneration should be evaluated not only by impurity removal but also by how strongly the leaching environment perturbs the sp^2 framework. Defect density and edge chemistry can directly influence interphase re-formation and long-term electrochemical stability [24,25], consistent with the route-dependent impedance response and depth-resolved surface-chemistry trends discussed in Sections 2.5 and 2.6.

2.4. Electrochemical Behavior of Regenerated Graphite in Half-Cells

Half-cell testing shows that, beyond impurity removal, the structural and near-surface states produced during regeneration can influence the polarization (overpotential) and cycling stability (Figure 4 and Table S2). SG shows limited reversible capacity and rapid fading, consistent with residual contaminants and a reactive, inhomogeneous surface that can sustain parasitic reactions and unstable interphase growth [32] (Figure 4a,c). In Figure 4a, SG reaches the upper cutoff voltage at a markedly lower capacity and shows a wider charge–discharge voltage hysteresis than the regenerated samples, indicating stronger polarization (larger lithiation/delithiation overpotential). The cyclic voltammograms show lower peak currents, broader lithiation/delithiation features, and an anodic peak shifted to higher potentials for SG (Figure 4b), consistent with slow interfacial kinetics. In contrast, the regenerated samples exhibit stronger and sharper redox features, and EG-H approaches CG (Figure 4a,b), suggesting the partial recovery of reversible interfacial kinetics. Regenerated samples recover capacity to near-commercial levels at early cycles: the initial discharge capacities are 350 (MG) and 346 mAh g^{−1} (EG), compared with 365 mAh g^{−1} for CG (0.1 C) (Figure 4a and Table S2). After heat treatment, the initial discharge capacities reach 362 (MG-H) and 365 mAh g^{−1} (EG-H). The initial Coulombic efficiencies also improve from 89% (SG) to 90% (MG/EG) and 92% (CG/MG-H/EG-H), which is consistent with the reduced irreversible Li consumption during the initial interphase formation [33].

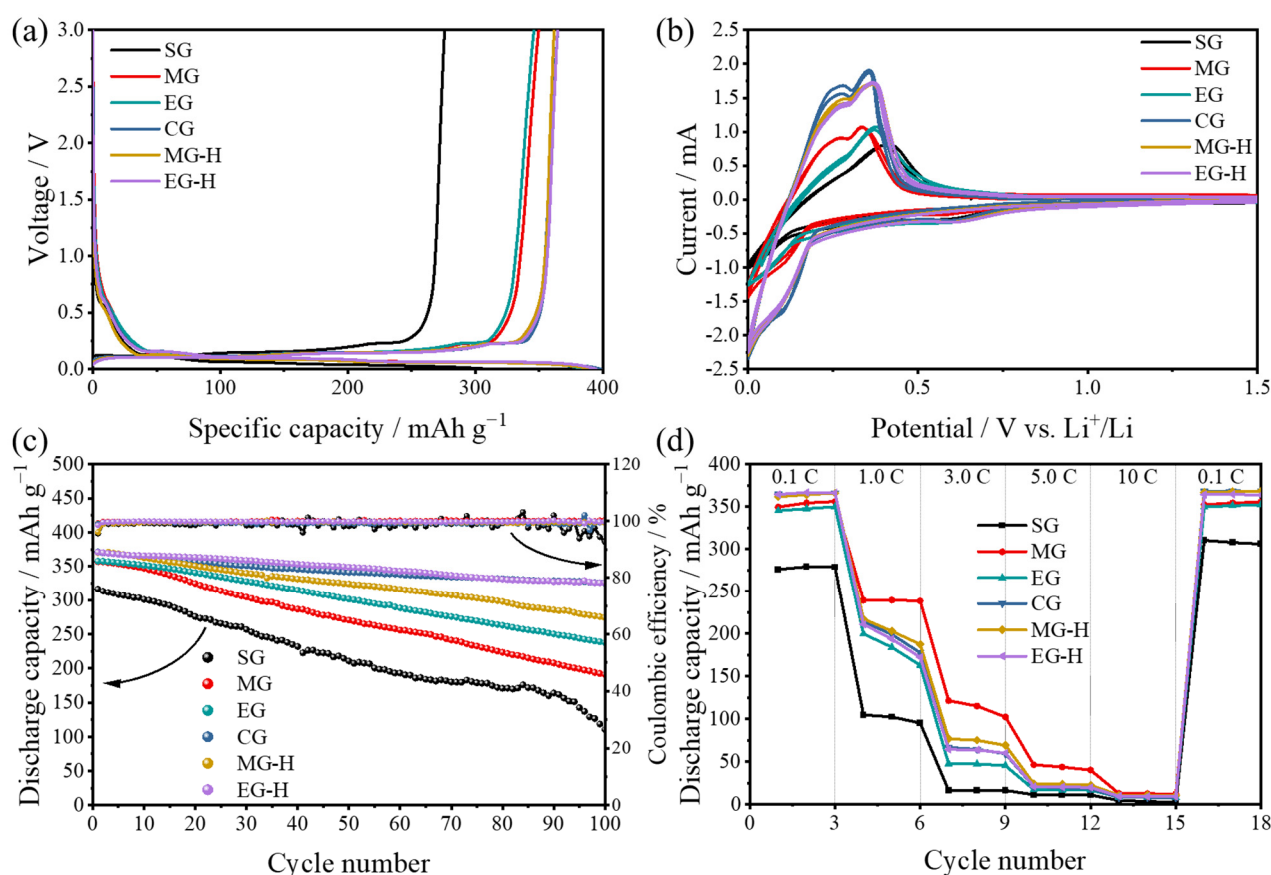


Figure 4. Half-cell electrochemical performance of SG, MG, EG, MG-H, EG-H, and CG: (a) galvanostatic charge–discharge profiles (0.1 C); (b) cyclic voltammograms (0.5 mV s^{−1}); (c) cycling performance (1.0 C, 100 cycles) and Coulombic efficiency; (d) rate capability (0.1–10 C).

Despite similar initial capacities, the cycling stability differentiates the routes. After 100 cycles, the capacity retention increases from 33% (SG) to 47% (MG) and 68% (EG),

and further to 70% (MG-H) and 87% (EG-H), comparable to that of CG (87%) (Figure 4c and Table S2). The rate capability further supports a polarization-limited response at high current densities: the discharge capacity decreases sharply at 1–10 C but largely recovers when the rate returns to 0.1 C (Figure 4d). This recovery indicates that the high-rate losses are largely reversible and dominated by polarization rather than by irreversible capacity loss. Within this polarization-limited regime, MG delivers higher discharge capacities at intermediate rates (1–5 C) than EG. Conversely, EG shows higher capacity retention during 1 C cycling (Figure 4c), highlighting a rate–lifetime trade-off between the two wet-chemical routes. This divergence indicates that the wet-processing environment can decouple short-term interfacial transport (rate capability) from long-term interphase passivation (capacity retention) once bulk impurities are largely suppressed.

This contrast is consistent with the malic-acid route yielding a leaching-conditioned near-surface state that is comparatively favorable for Li^+ transport at elevated rates, but less passivating over extended cycling. In contrast, alkaline chelation combined with a heat treatment tends to suppress defect-driven side reactions that promote continued interphase growth. The separation between MG and EG, and between MG-H and EG-H, is observed even though bulk impurity levels are already comparable by ICP–MS. These trends are consistent with a surface-controlled mechanism once bulk contaminants are suppressed as a dominant variable. This interpretation is further supported by the EIS analysis (Section 2.5) and the depth-resolved XPS results (Section 2.6), which are discussed in the following subsections. Acidic processing may leave a more defect-rich and oxygenated near-surface region, thereby facilitating continued SEI growth and increasing the impedance during cycling [24,25]. In contrast, alkaline chelation tends to preserve structural integrity and yields a near-surface state that is more favorable for stable SEI re-formation after a heat treatment. Therefore, the electrochemical data indicate that regeneration routes should be evaluated based on the structure and near-surface state, as well as purification, because the dominant degradation mode can shift to interphase-controlled loss once transition-metal contaminants are largely removed [34,35].

2.5. Interfacial Resistance and Kinetic Parameters from Electrochemical Impedance Spectroscopy

EIS Nyquist plots (Figure 5a) exhibit a high-frequency semicircle and low-frequency diffusion tail. The spectra are collected after the formation cycling and are stabilized at 0.7 V (Section 3.5); therefore, the fitted parameters primarily reflect the nascent interphase formed on each regenerated surface. The spectra are fitted using the equivalent circuit $R_S-(R_{SEI}\parallel CPE_{SEI})-(R_{CT}\parallel CPE_{CT})-W_O$ (Figure 5c) [36,37]. In this circuit, “ $\parallel$ ” denotes a parallel combination. R_S represents the uncompensated ohmic resistance (electrolyte, separator, and contact contributions), R_{SEI} the SEI resistance, and R_{CT} the charge-transfer resistance. CPE_{SEI} and CPE_{CT} are constant phase elements that describe the nonideal capacitive behavior, and W_O is the Warburg element capturing the diffusion-related response. Table 1 summarizes R_{SEI} , R_{CT} , and their sum ($R_{SEI} + R_{CT}$). Because porous/heterogeneous composite electrodes typically exhibit depressed semicircles (i.e., nonideal capacitive response), CPE terms are used here to capture the distribution of relaxation times and to obtain stable fits. Accordingly, the extracted resistances should be regarded as effective (model-dependent) parameters, and the discussion focuses on trends that are also apparent from the raw Nyquist semicircle sizes (Figure 5a,b) and from the total interfacial resistance ($R_{SEI} + R_{CT}$) summarized in Table 1.

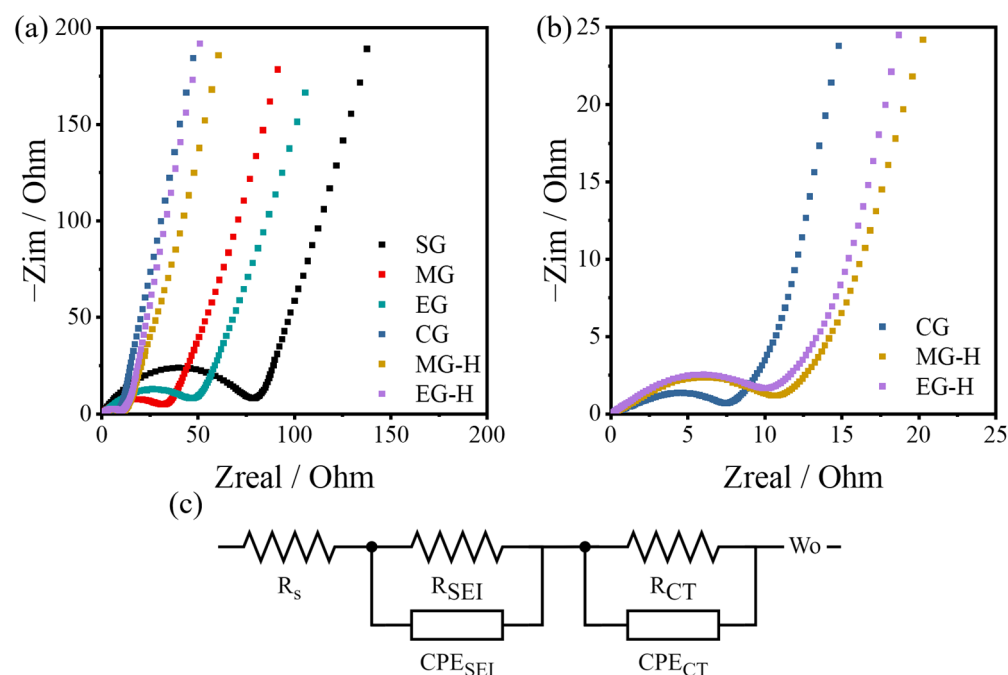


Figure 5. Electrochemical impedance spectroscopy (EIS) analysis and equivalent-circuit fitting: (a) Nyquist plots of SG, MG, EG, CG, MG-H, and EG-H; (b) enlarged view for CG, MG-H, and EG-H; (c) equivalent circuit used for fitting ($R_s - (R_{\text{SEI}} \parallel \text{CPE}_{\text{SEI}}) - (R_{\text{CT}} \parallel \text{CPE}_{\text{CT}}) - W_O$). Abbreviations: R_s , ohmic resistance; R_{SEI} , solid electrolyte interphase (SEI) resistance; R_{CT} , charge-transfer resistance; CPE, constant phase element (CPE_{SEI} and CPE_{CT} correspond to SEI- and charge-transfer-related CPE terms, respectively); W_O , Warburg element.

Table 1. Fitted interfacial resistances (R_{SEI} and R_{CT}) and their sum ($R_{\text{SEI}} + R_{\text{CT}}$) from electrochemical impedance spectroscopy (EIS) (Figure 5c) for SG, MG, EG, CG, MG-H, and EG-H (R_{SEI} , solid electrolyte interphase (SEI) resistance; R_{CT} , charge-transfer resistance).

Sample	R_{SEI}/Ω	R_{CT}/Ω	$R_{\text{SEI}} + R_{\text{CT}}/\Omega$
SG	46.7	33.2	79.9
MG	12.4	19.8	32.2
EG	24.8	23.1	47.9
CG	5.7	1.8	7.5
MG-H	7.8	2.9	10.7
EG-H	6.4	3.7	10.1

The fitted parameters quantify the effect of regeneration on these contributions. SG exhibits the largest impedance response, with an enlarged semicircle and extended low-frequency tail (Figure 5a), indicating large SEI and charge-transfer resistances. SG consistently shows the highest fitted R_{SEI} and R_{CT} values (Table 1). Both wet-chemical routes reduce these resistances, and the heat treatment yields the responses closest to the commercial benchmark, as highlighted by the enlarged low-impedance view (Figure 5b). The SEI resistance (R_{SEI}) decreases from 46.7 Ω (SG) to 12.4 Ω (MG) and 24.8 Ω (EG), and further to 7.8 Ω (MG-H) and 6.4 Ω (EG-H), compared with 5.7 Ω for CG. A parallel trend is observed for the charge-transfer resistance (R_{CT}) (33.2, 19.8, 23.1, 2.9, 3.7, and 1.8 Ω for SG, MG, EG, MG-H, EG-H, and CG, respectively). The fitted $R_{\text{SEI}} + R_{\text{CT}}$ follows the same order (79.9, 32.2, 47.9, 10.7, 10.1, and 7.5 Ω for SG, MG, EG, MG-H, EG-H, and CG, respectively). Notably, MG-H and EG-H exhibit very similar low resistances close to CG; therefore, their

small numerical difference at the measurement point (0.7 V) is treated as comparable within fitting uncertainty and does not affect the main conclusions.

The fitted parameters show that the heat treatment substantially reduces the interfacial resistance, aligning with an interphase formed in a less reactive and better-ordered near-surface state. This interpretation is supported by the heat-treatment-driven decrease in the oxygenated carbon contributions and accompanying shift in the SEI-relevant near-surface speciation observed by depth-resolved XPS (Section 2.6). The extracted resistances are effective parameters within the chosen circuit, and are used to compare samples measured under identical conditions.

In addition, although MG exhibits a lower R_{SEI} than EG at the measurement point (Table 1), EG exhibits a higher long-term retention, indicating that early-stage impedance does not fully capture the subsequent interphase evolution [38]. This comparison suggests that a slightly more resistive initial film can be more passivating, thereby suppressing continued electrolyte decomposition and limiting the deleterious interphase growth during cycling [39,40]. Accordingly, the impedance trends are interpreted in conjunction with the depth-resolved XPS results to relate the resistance behavior to near-surface speciation, which biases SEI formation and its evolution during cycling.

2.6. Depth-Resolved Surface Chemistry and SEI-Relevant Species

XPS depth profiling links the regeneration environment to the SEI-relevant near-surface speciation [41,42]. The depth profiles are acquired from the electrodes harvested after the third formation cycle. Therefore, the profiles reflect the nascent SEI on each regenerated graphite surface. Here, ‘etching time’ refers to the cumulative Ar⁺ sputter-etching duration used for XPS depth profiling (0–720 s) (Figures 6 and 7). The quantified relative fractions summarized in Figures 6 and 7 are obtained from the peak deconvolution of the corresponding high-resolution spectra; representative peak-fitting results are provided in Figure S1 (MG and EG) and Figure S2 (MG-H and EG-H). Sputter yields depend on the matrix and Ar⁺ sputtering can perturb labile interphase components; therefore, the etching time is used as a relative depth coordinate. The profiles are discussed primarily as relative trends under identical sputtering conditions.

Clear route-dependent trends emerge in the C 1s-derived speciation under identical sputtering conditions. MG exhibits a more oxygenated outermost layer, where the graphite component is 28% and the C=O content reaches 49% at an etching time of 0 s (Figure 6a). In contrast, EG exhibits a higher graphite fraction (32%) and lower C=O fraction (38%) at 0 s (Figure 6b). The heat treatment increases the graphite contribution at the outermost surface for both routes: MG-H reaches 40% graphite and 24% C=O at 0 s (Figure 6c), whereas EG-H reaches 49% graphite and 22% C=O (Figure 6d). As the etching time increases, the graphite fraction increases in all cases (e.g., from 28% to 42% for MG and from 49% to 56% for EG-H; Figure 6a,d), indicating that an oxygen-containing layer is concentrated near the surface where SEI formation is initiated [42–44]. For EG-H, C=O remains in a narrow range (~22–24%), whereas COOH and “Other” decrease with etching time (Figure 6d). A similar decrease is observed for MG-H (COOH: 17% at 0 s → 10% at 720 s; Figure 6c), indicating that the O–C=O (COO–/COOH) contribution is concentrated near the outermost surface and is progressively attenuated as the graphite signal becomes dominant with etching time. Thus, the total oxygenated fraction decreases overall despite the relatively stable C=O contribution. Within the XPS-information depth, a lower graphite fraction at 0 s reflects stronger attenuation by an oxygenated overlayer (e.g., SEI or residual surface species), whereas a higher graphite fraction suggests a thinner or less oxygen-rich near-surface layer. This interpretation is consistent with the improved initial Coulombic efficiencies after heat treatment (Section 2.4), suggesting reduced irreversible Li consumption during formation.

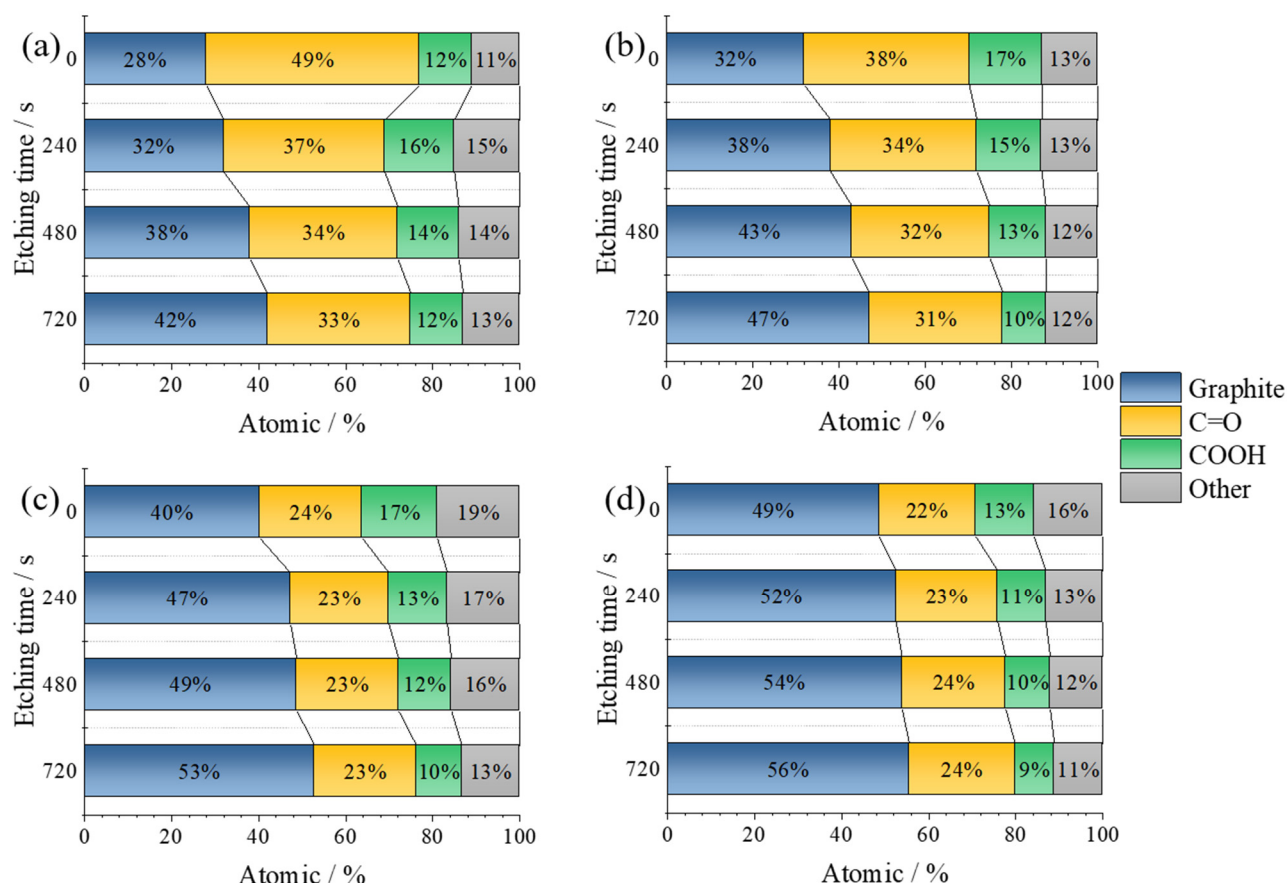


Figure 6. Depth-resolved carbon speciation from C 1s X-ray photoelectron spectroscopy (XPS): relative fractions (peak-area fractions) of graphite, C=O, COOH (O–C=O/COO–), and other components versus Ar+ sputter-etching time (0–720 s) for (a) MG, (b) EG, (c) MG-H, and (d) EG-H.

Li-containing speciation further differentiates the routes (Figure 7). MG exhibits a substantial LiOH contribution at the outermost surface (16% at 0 s), which decreases with increasing etching time (8% at 720 s) (Figure 7a). The elevated LiOH fraction at the outermost surface is consistent with the more reactive near-surface chemistry, indicating that the nascent interphase is less carbonate-dominated in the early stages. LiOH has been reported to promote a compositional transformation of organic SEI components, where lithium ethylene di-carbonate (LEDC) is converted to lithium ethylene mono-carbonate (LEMC) with concomitant Li_2CO_3 formation ($\text{LEDC} + \text{LiOH} \rightarrow \text{LEMC} + \text{Li}_2\text{CO}_3$) [45]. Because LEMC is relatively soluble, this transformation can fragment or partially dissolve the initial SEI, increasing electrolyte access to fresh graphite surface and thereby promoting continuous SEI re-formation. By contrast, EG exhibits a Li_2CO_3 -dominated profile (83% at 0 s), whereas LiOH accounts for 7% at 0 s and remains as a minor component (Figure 7b). A carbonate-dominated (Li_2CO_3 -rich) interphase with low LiOH is therefore expected to be more passivating and less prone to dissolution-driven re-formation, consistent with the more stable interfacial behavior observed for the alkaline route. After heat treatment, the LiOH fraction decreases in MG-H and remains low in EG-H (Figure 7c,d), whereas the carbonate-dominated compositions persist. ROCO_2Li and the apparent Li_2O contribution become more evident at longer etching times, particularly after heat treatment. Notably, Figure 7 is normalized within the Li-containing speciation set, whereas the COOH (O–C=O/COO–) fraction in Figure 6 is normalized to the total C 1s signal; therefore, the ROCO_2Li trend does not need to mirror the COOH depth trend. Ar+ sputtering can modify fragile SEI components; therefore, the Li_2O trend is interpreted conservatively.

as a depth-dependent increase in the more inorganic inner-layer signal, rather than as a strictly quantitative thickness-resolved phase map. However, the consistent increase in the inorganic fraction with etching time is compatible with a carbonate-rich outer region and a more inorganic inner region within the nascent interphase.

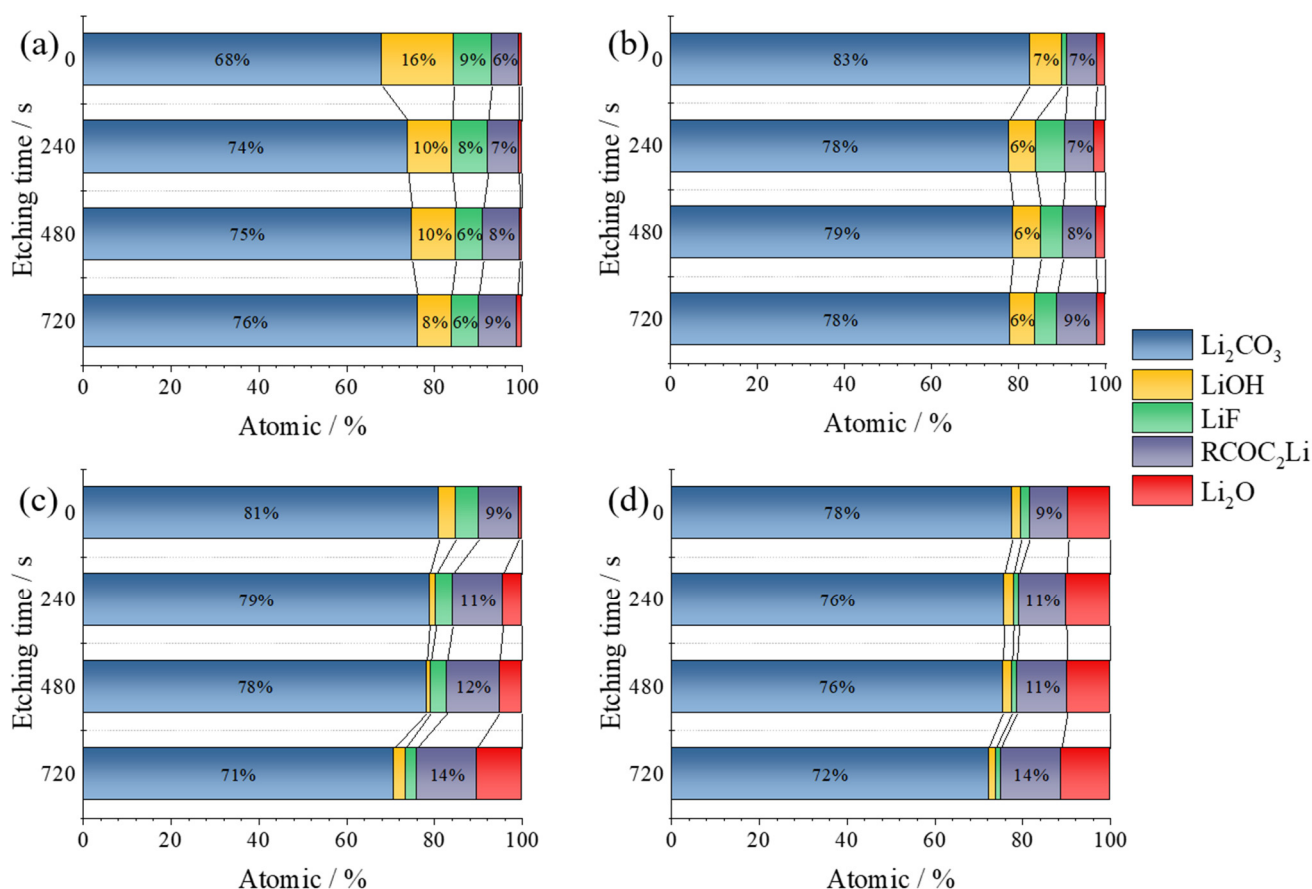


Figure 7. Depth-resolved Li speciation from XPS: relative fractions (peak-area fractions) of Li₂CO₃, LiOH, LiF, ROCO₂Li, and Li₂O versus Ar⁺ sputter-etching time (0–720 s) for (a) MG, (b) EG, (c) MG-H, and (d) EG-H.

These compositional differences provide a chemical basis for the electrochemical hierarchy. The oxygenated carbon functionalities and LiOH-rich species indicate a more reactive near-surface environment. Such a surface can promote electrolyte decomposition and destabilize organic carbonate-derived interphase components, favoring continued SEI growth [45]. In particular, LiOH can drive the LEDC → LEMC transformation and associated SEI destabilization, which leads to repeated electrolyte–electrode contact and incessant SEI dissolution/re-formation [45]. This continuous re-formation pathway provides a mechanistic basis for the progressive impedance growth and irreversible Li consumption observed during cycling when the outermost surface is LiOH-rich. Together, these features provide a plausible pathway for the continued irreversible Li consumption and progressive impedance growth during cycling. This interpretation is consistent with the higher density of polar defect/edge sites [10,24,25]. These sites can shift the interphase reactions away from the carbonate-dominated compositions during formation and contribute to the increase in resistance during cycling. By contrast, a more graphitic and carbonate-rich near-surface composition is associated with lower interfacial resistance and more stable cycling, particularly after heat treatment [46]. The depth-resolved analysis suggests that regeneration effectively conditions the surface state prior to formation, thereby biasing

the subsequent SEI chemistry and evolution. Once bulk impurities are minimized to near-commercial levels, the electrochemical recovery becomes more sensitive to the chemical state and defect structure in the outermost near-surface region. These features can influence SEI re-formation and impedance evolution. More broadly, stable ion-conducting interphases and interface/interphase regulation are widely recognized as key determinants of long-term stability across rechargeable battery chemistries [47,48].

3. Materials and Methods

3.1. Materials and Sample Preparation

SG was provided by the Korea Automotive Technology Institute (Cheonan, Chungnam, Republic of Korea). The material was recovered from cylindrical Li-ion cells after long-term cycling when the discharge capacity decreased to 86% of its initial value. The residual energy was removed by fully discharging the cells in brine solution. The cells were mechanically dismantled to separate the positive and negative electrodes. The isolated negative-electrode sheets were crushed, and the organic binder was removed by thermal debinding at 600 °C for 30 min under a nitrogen atmosphere, yielding SG powder for subsequent regeneration. This 600 °C step was used only for binder removal prior to regeneration and is distinct from the 1200 °C post-treatment applied after wet-chemical regeneration (Section 3.3). In this study, ‘SG’ denotes spent graphite after binder removal. After debinding, the inorganic residues and metallic impurities remained detectable, as confirmed by ICP–MS (Section 3.6). CG (CGB-10; Nippon Graphite Industries, Ltd., Otsu, Shiga, Japan) was used as the reference material.

Deionized water (HPLC grade; Honeywell Burdick & Jackson, Morris Plains, NJ, USA) was used to prepare all aqueous solutions. DL-malic acid (99+%; Thermo Fisher Scientific, Waltham, MA, USA) was dissolved in deionized water to prepare a 1.0 mol dm^{−3} solution (pH 2.2). EDTA (99.4–100.6%; Merck KGaA, Darmstadt, Hessen, Germany) was prepared as a 0.5 mol dm^{−3} aqueous solution. Because the solubility of EDTA increases under alkaline conditions, sodium hydroxide pellets (≥97.0%; Merck KGaA, Darmstadt, Hessen, Germany) were added to adjust the solution to pH 8.7. D-(+)-glucose (99%; Thermo Fisher Scientific, Waltham, MA, USA) was used as the reducing agent via the malic-acid route (Section 3.2).

3.2. Wet-Chemical Regeneration (Malic Acid and EDTA)

Wet-chemical regeneration was performed via malic-acid leaching under acidic conditions and EDTA chelation under alkaline conditions (pH 8.7). The overall workflow and sample nomenclature are shown in Figure 8. SG was subjected to either malic-acid leaching or EDTA chelation. After washing with deionized water and vacuum-drying, MG and EG were obtained, respectively. The dried powders were further heat-treated to produce MG-H and EG-H (Section 3.3).

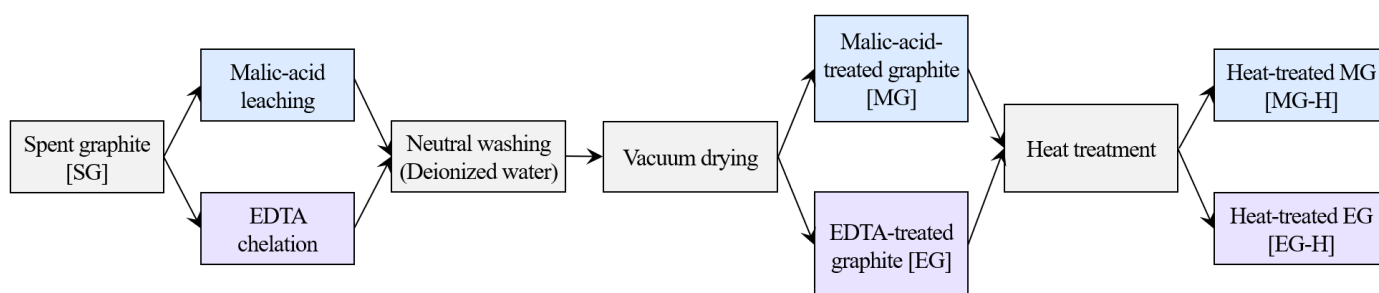


Figure 8. Schematic of the wet-chemical regeneration (malic-acid leaching and EDTA chelation) and sample nomenclature.

For direct comparison between the two routes, the same solid-to-liquid ratio, reaction temperature, and holding time were applied in both cases. The reagent concentrations were selected based on literature-reported operating conditions for each route rather than matching the molarity between malic acid and EDTA. For the malic-acid route, the malic-acid concentration (1.0 mol dm^{-3} , pH 2.2) and associated process variables (solid-to-liquid ratio, temperature, holding time, and glucose dosage) were adopted based on the optimized conditions reported in Ref. [49]. For the EDTA route, the EDTA concentration (0.5 mol dm^{-3}) was selected based on prior EDTA-based leaching literature (Ref. [17]) reporting 0.5 mol dm^{-3} as an effective concentration under comparable leaching time and temperature. Glucose was added only in the malic-acid route to provide a reducing environment. In weak organic-acid leaching systems, glucose can promote the reductive dissolution of transition-metal-bearing residues by reducing higher-valence species to more soluble lower-valence states, thereby facilitating dissolution and complexation under weak-acid conditions [49]. The reducing environment was also intended to mitigate oxidative side reactions (oxidative functionalization/etching) on the graphite surface during malic-acid treatment. Sodium hydroxide was used to adjust the EDTA solution to pH 8.7. Leaching experiments were performed in a three-neck reactor equipped with a reflux condenser to minimize solvent loss during heating. The slurry was agitated and heated using a stirring mantle (MS-DMSDB; Misung Scientific, Yangju, Gyeonggi, Republic of Korea). After treatment, the resulting slurry was subjected to the post-processing steps described in Section 3.3.

For acidic leaching, SG was dispersed in a 1.0 mol dm^{-3} malic-acid solution (pH 2.2) at a solid-to-liquid ratio of 25 g dm^{-3} . The mixture was heated to 90°C with continuous agitation and maintained at 90°C for 120 min under reflux. D-(+)-glucose powder (99%; Thermo Fisher Scientific, Waltham, MA, USA) was added at 0.5 g per 1 g of SG, 30 min after the slurry reached 90°C to introduce a reducing environment during the malic-acid treatment.

For EDTA chelation under alkaline conditions, SG was dispersed in a 0.5 mol dm^{-3} EDTA solution adjusted to pH 8.7 and treated at the same solid-to-liquid ratio (25 g dm^{-3}). The slurry was heated to 90°C under agitation and held at 90°C for 120 min under reflux using the same reactor configuration and heating/stirring setup as for the acidic leaching route.

3.3. Post-Treatment: Washing, Drying, and Heat Treatment

After the leaching/chelation step (Section 3.2), post-treatment (washing, vacuum drying, and heat treatment) was performed, as shown in Figure 8. After the wet-chemical step, the graphite suspensions were cooled to room temperature and the solids were collected via vacuum filtration. The collected powders were washed thoroughly with deionized water to remove the residual leachant and dissolved species. The washed powders were dried in a vacuum oven at 80°C for 8 h to obtain MG and EG (Figure 8).

A high-temperature (1200°C) treatment was then applied to restore the graphitic ordering and reduce defect-associated reactivity. Dried MG and EG powders were placed in an alumina boat and heat-treated in a tube furnace (HTF-Q60; Hantech, Gunpo, Gyeonggi, Republic of Korea) under flowing argon (0.7 L min^{-1}). The furnace temperature was increased to 1200°C and maintained for 120 min; the samples were then allowed to cool naturally to room temperature under Ar. The heat-treated products are denoted as MG-H and EG-H (Figure 8). Direct heat treatment of impurity-rich SG without prior wet leaching was not pursued in this work. Because SG contains cathode-derived transition-metal residues that can exist as oxides, high-temperature treatment ($\geq 1000^\circ\text{C}$) may induce carbothermal reduction (e.g., $\text{MO}_x + x\text{C} \rightarrow \text{M} + x\text{CO}\uparrow$), which can directly consume carbon and introduce additional defects/porosity. Therefore, the 1200°C post-treatment was

applied after wet impurity removal to focus on lattice/ordering recovery rather than impurity-driven carbon consumption.

3.4. Electrode Fabrication and Cell Assembly

Working electrodes were prepared using graphite powders (SG, MG, EG, MG-H, EG-H, and CG) as active materials. N-methyl-2-pyrrolidone (NMP; 99.0% purity; Junsei Chemical, Tokyo, Japan) was used as the solvent. PVDF (average molecular weight: ~534,000; Merck KGaA, Darmstadt, Hessen, Germany) was dissolved in NMP to obtain a 12 wt.% binder solution. Each graphite powder sample was mixed with PVDF at a mass ratio of 9:1 in a planetary mixer (ARM-310; Thinky Corporation, Tokyo, Japan) at 2000 rpm for 15 min to form a homogeneous slurry. No conductive additives were used. The slurry was cast onto copper foil current collectors (18 μm ; UACJ Corporation, Tokyo, Japan) using a doctor blade with a 0.1 mm gap, then vacuum-dried at 120 $^{\circ}\text{C}$ for 8 h. The dried electrodes were punched into disks (15.95 mm diameter) using a punch (WC-H125; Wellcos, Gunpo, Gyeonggi, Republic of Korea).

Cells were assembled in an Ar-filled glove box (SK-G1200; Three-Shine, Yuseong, Daejeon, Republic of Korea; dew point below -70°C). Two-electrode CR2032 coin cells were assembled using the graphite electrode as the working electrode, polypropylene separators (Celgard A273; 16 μm ; Celgard LLC, Charlotte, NC, USA), and Li metal foil (500 μm ; Vitzrocell, Dangjin, Chungnam, Republic of Korea) as the counter/reference electrode. The electrolyte was 1 mol dm^{-3} LiPF_6 in ethylene carbonate/ethyl methyl carbonate (EC:EMC = 1:1, v/v) (battery grade; Duksan Electera, Gongju, Chungnam, Republic of Korea). For measurements requiring a three-electrode configuration, an additional Li metal foil was used as the reference electrode under otherwise identical separator and electrolyte conditions.

3.5. Electrochemical Characterization

Galvanostatic charge–discharge, rate capability, and cycling stability tests were performed in two-electrode CR2032 coin cells using a battery-test system (WBCS 3000; WonATech, Seoul, Republic of Korea). The C-rate was defined based on the theoretical capacity of graphite (1.0 C = 372 mA g^{-1}), and the current was normalized to the mass of the graphite active material in the working electrode. After cell assembly, a 10 h rest period was applied for electrolyte wetting. Formation cycling was conducted at 0.1 C, comprising charging to 0.0 V (vs. Li^+/Li), a 5 min rest, and discharging to 3.0 V (vs. Li^+/Li). This procedure was repeated three times. The lower cutoff voltage (0.0 V vs. Li^+/Li) was selected to approach near-complete lithiation of graphite and to apply a consistent lithiation endpoint across samples. To minimize possible Li deposition at very low potentials, formation was conducted at a low rate (0.1 C). Rate-capability testing was performed starting from the fourth cycle over the same voltage window (3.0–0.0 V vs. Li^+/Li) with the rate stepped sequentially to 1.0, 3.0, 5.0, 10, and 0.1 C. After the rate testing, long-term cycling was performed for 100 cycles. Each cycle consisted of constant-current charging at 1.0 C to 0.0 V, followed by a constant-voltage hold at 0.0 V until the current decreased to 0.01 C. The constant-voltage step was terminated at 0.01 C to avoid prolonged polarization at the lower cutoff. This condition also ensured comparable end-of-charge states across samples. After a 5 min rest period, constant-current discharging was carried out at 1.0 C to 3.0 V.

To complement the galvanostatic testing and investigate the redox features and interfacial kinetics, cyclic voltammetry and EIS were conducted using an electrochemical workstation (ZIVE MP2A; WonATech, Seoul, Republic of Korea). Cyclic voltammetry was recorded over 3.0–0.0 V (vs. Li^+/Li) at a scan rate of 0.5 mV s^{-1} for three cycles. Electrochemical impedance spectra were obtained at 0.7 V (vs. Li^+/Li) using a sinusoidal

perturbation of 5 mV across a frequency range of 100 kHz to 0.01 Hz, after formation cycling and a stabilization hold at 0.7 V. Impedance spectra were analyzed by equivalent-circuit fitting to extract interfacial parameters, including R_{SEI} and R_{CT} .

3.6. Structural and Surface Characterization

Residual Li and transition-metal impurities (e.g., Co, Ni, and Mn) were quantified using ICP-MS (7700x; Agilent Technologies, Santa Clara, CA, USA). For analysis, a known mass of each graphite sample was digested in aqua regia using a microwave digestion system (UltraWAVE; Milestone, Sorisole, Bergamo, Italy) at 220 °C for 30 min, and the resulting solution was introduced into the ICP-MS for elemental quantification. Because the target analytes are inorganic/metal impurities rather than the graphite carbon framework, the digestion step was used to solubilize the metallic and inorganic residue fraction for bulk impurity quantification. The morphology and surface features of the graphite particles were examined using FE-SEM (SIGMA 360; Carl Zeiss AG, Oberkochen, Baden-Württemberg, Germany). Elemental distributions and qualitative compositional information were obtained using EDS (XFlash 7; Bruker Corporation, Billerica, MA, USA) coupled with FE-SEM.

The crystal structure and interlayer spacing were evaluated by XRD (MiniFlex 600; Rigaku, Tokyo, Japan) using Cu K α radiation at 40 kV and 15 mA. The (002) reflection was analyzed to determine the interlayer spacing (d_{002}) and assess the changes in graphitic ordering induced by wet processing and subsequent heat treatment. Structural disorders were assessed by Raman spectroscopy (RAMANtouch; Nanophoton Corporation, Osaka, Japan). The defect-related D band and graphitic G band were analyzed, and the A_D/A_G ratio was calculated from the relative peak areas to compare the defect densities among the samples.

The near-surface chemical states were analyzed using XPS (K-Alpha+; Thermo Fisher Scientific, East Grinstead, West Sussex, UK) with Ar+ sputter depth profiling. To probe the surface layers relevant to the initial SEI formation, graphite electrodes were harvested after the third formation cycle (0.1 C, three cycles; Section 3.5) and examined using XPS. Electrodes were harvested and transferred for XPS to minimize air exposure. The harvested electrodes were gently rinsed with anhydrous dimethyl carbonate to remove the residual electrolyte and were vacuum-dried prior to analysis. High-resolution spectra were acquired at etching times of 0, 240, 480, and 720 s, where the etching time denotes the Ar+ sputtering time used for XPS depth profiling. The C 1s spectra were deconvoluted into graphite, C=O, COOH, and other components, and the Li-containing compounds were quantified by fitting the contributions of Li_2CO_3 , LiOH, LiF, $ROCO_2Li$, and Li_2O to construct depth-resolved speciation profiles (Figures 6 and 7). The representative peak-fitting results are shown in Figures S1 and S2. Depth profiles are presented versus Ar+ sputter-etching time (0–720 s), and the comparisons focus on relative trends under identical sputtering conditions across samples.

4. Conclusions

Spent negative-electrode graphite recovered from cylindrical Li-ion cells was regenerated via malic-acid leaching under acidic conditions (pH 2.2) and EDTA chelation under alkaline conditions (pH 8.7). This was followed by a high-temperature step (1200 °C) to promote graphitic ordering and mitigate the defect-associated reactivity. Under matching conditions, both wet-chemical routes reduced the bulk impurity level from >200 ppm to ~2 ppm, indicating that comparable bulk purification could be achieved. Depth-resolved XPS after formation cycling revealed route-dependent near-surface states relevant to SEI re-formation that seed early interphase chemistry: the acid-processed graphite exhibited a higher LiOH contribution at the outermost surface (~16% vs. ~7%) and more

oxygenated carbon components, whereas the alkaline route favored a more graphitic, carbonate-dominated near-surface composition consistent with a less oxygen-rich, more passivating surface condition after formation.

Electrochemical testing and impedance fitting were consistent with these surface differences, and the alkaline route after the high-temperature step approached the interfacial resistance behavior of the commercial reference, while recovering the commercial-level capacity retention (87% after 100 cycles). Overall, the results indicate that electrochemical recovery depends on both bulk purification and the leaching-conditioned near-surface chemical state and defect structure. This biases the SEI composition and resistance evolution during cycling; that is, once transition-metal contaminants are largely suppressed, performance is governed primarily by surface-conditioned interphase stability rather than by bulk purity alone. Accordingly, regeneration routes should be selected not only for impurity removal efficiency but also for how they precondition the near-surface state toward stable (passivating) SEI chemistry while limiting defect/oxidation-driven reactivity. Future studies should validate these relationships using full-cell configurations with practical areal loadings. In addition, a glucose-free control for the malic-acid route and dedicated verification of leaching-stage redox effects will be valuable to further decouple the role of glucose from pH/complexation effects. Systematic concentration optimization will also be beneficial to minimize reagent consumption. Process-level evaluations should also address the energy demand of the high-temperature step and practical strategies for managing or recycling spent leachates.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ijms27052322/s1>.

Author Contributions: Y.C.: writing—original draft, methodology, formal analysis, data curation, conceptualization. S.L.: formal analysis, conceptualization. S.Y.: methodology, formal analysis. S.-K.J.: writing—review and editing, supervision, funding acquisition, formal analysis, data curation, conceptualization. All authors have read and agreed to the published version of the manuscript.

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