Quantifying Redox Orbital Coupling to the Carbon Nano-circuitry in Battery Cathodes with Electron-Positron Momentum Density Mapping

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Coincidence Doppler Broadening spectroscopy is a powerful tool for quantitatively analyzing the coupling of redox orbitals in $LiCoO_2$ microparticles with the carbon binder domain embedded in battery cathodes, utilizing Electron-Positron Momentum Density Mapping. This approach overcomes the limitations of X-ray Compton scattering, which often faces challenges due to small cross sections. From the calculated Doppler profiles of $LiCoO_2$ and different carbon nanostructures, we fit the measured Doppler profile to extract the contributions of $LiCoO_2$ and the p conducting orbital of two-dimensional carbon nanostructures such as graphene flakes and carbon nanocages or nanotubes. This carbon contribution measures the coupling existing between the redox center and the conducting channels within the nanocircuitry of the cathode. This approach provides an efficient method to effectively uncover fast conducting channels hidden within the cathode materials. Our findings deepen understanding of nano-engineered battery optimization for cathode functionality.

Positron Annihilation Spectroscopy (PAS) represents a powerful detection technology [1–3] widely used for identifying, quantifying, and mapping defects within crystalline structures and has been extensively and successfully applied across various fields including light alloys [4], semiconductors [5], and next-generation photovoltaic (PV) devices [6]. The phenomenon of positron trapping can be identified by changes in the momentum distribution of the annihilation radiation, which indicates the local electronic environments encountered by positrons. The Coincidence Doppler Broadening (CDB) technique, which uses dual gamma-ray spectrometers to detect coincident annihilation photons, has proven to be particularly adept at revealing the chemical surroundings of high-momentum positron traps. This sensitivity extends to elucidating the motion of electron-positron pairs observed in the laboratory reference frame [7]. The chemical fingerprints provided by fast electrons at the annihilation sites offer crucial insights into the material's chemical composition. Combining high-quality experiments with modeling, particularly the two-component Density Functional Theory (DFT) [8] for electron-positron systems, allows for a reliable interpretation of these associations. This approach has become indispensable for simulating positron annihilations in delocalized states or open-volume defects within solid systems.

The demand for batteries with higher specific capacities and longer lifetimes, without compromising safety, continues to grow in modern society. Recently, the application of positron spectroscopy in advanced energy fields has garnered significant attention, such as the detection of quantum dots in solar cells by team xxx. Here, we specifically focus on alkali-ion batteries, particularly lithium-ion batteries, using $LiCoO_2$ (LCO) as a case study. Since its introduction as a cathode material in 1980, the capacity of LCO has typically been limited to half its theoretical value of 140 mAh/g. However, recent studies on doping, coating, and redox processes have shown that up to 0.7 Li corresponding to 200 mAh/g can be reversibly used, underscoring the indispensable role of anionic redox reactions (ARR) in enhancing capacity. These studies highlight the importance of precise detection technologies for redox pathways.

Traditional methods such as X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), and X-ray photoelectron spectroscopy (XPS) have been widely used for probing redox pathways, but they often encounter issues such as shallow probe depths and entangled signals that hinder reliable assessments and analysis. Interestingly, the technique of resonant inelastic X-ray scattering (mRIXS) enables the direct observation of oxygen redox states in LCO, thereby enhancing our understanding of these reactions. It is noteworthy that positron methods elegantly complement the shortcomings of traditional X-ray techniques. The Coincidence Doppler Broadening (CDB) technique allows for deep probing into the material to detect changes in the momentum space density distribution associated with positron annihilation, which is crucial for understanding the interfaces of cathode materials in alkali-ion batteries.

In this study, we employ CDB to highlight the significance of redox pathways and the momentum spectral information of various carbon-coated cathode materials. Theoretical calculations are utilized to fit and replicate
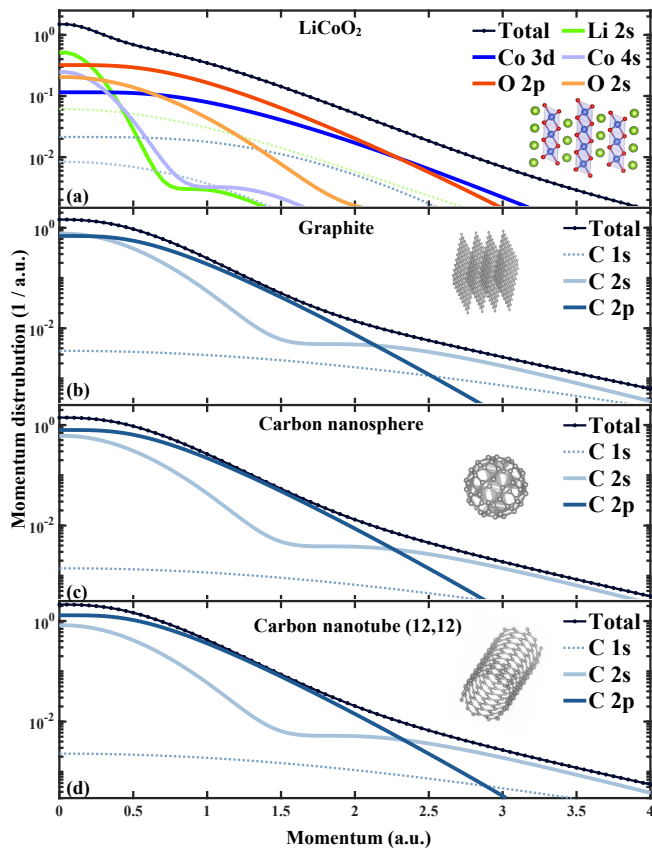
FIG. 1. Computed Doppler spectra for (a) LiCoO$_2$ and (b-d) various types of graphite. The complete spectra are depicted with black solid lines. (a) LiCoO$_2$, the valence orbitals of Li, Co, and O are represented by green, blue, and orange solid lines, respectively, with their corresponding core orbitals shown using matched dashed lines. (b), (c), (d) show the graphite, nanosphere (C60), nanotube (CNT-12), respectively. Valence orbitals are shown in solid lines, and contributions from core electrons are indicated with dashed lines. Different electronic orbital contributions are distinguished by color coding.

experimental positron annihilation spectra, leveraging momentum information from electron-positron interactions to underscore the efficacy of positrons as amplifying antimatter probes. Additionally, we introduce a novel modeling framework that demonstrates the selective sensitivity of positrons within crucial orbital pathways of battery electrodes. By simulating different topological structures, this research illustrates the selective capabilities of positron technology in carbon-based topologies. Ultimately, this synergy of theory and experiment not only proves viable for battery applications but also paves the way for the use of carbon-based materials in applications like superconductivity and alloys.

METHODS

A first-principles approach via the Vienna Ab initio Simulation Package (VASP) [9] were used to calculate the bulk systems. We utilized the Projector Augmented Wave (PAW) method [10] and the Perdew–Burke–Ernzerhof (PBE) electron-electron exchange and correlation functional [11], which are integral to the Generalized Gradient Approximation (GGA) [12] applied during the relaxation processes. To account for the Coulombic interactions in the localized d electrons of cobalt ions, we applied the GGA + U method [13], incorporating a Hubbard-type U term (U − J = 3.3 eV) [14]. A plane-wave cutoff energy of 400 eV effectively ensured convergence and we utilized a Γ-centered Monkhorst-Pack $9 \times 9 \times 1$ k-mesh [15] for LCO with Gaussian smearing set at 0.2 eV. The optimized LCO hexagonal cell with a and c parameter values were calculated to be 2.81 Å, 13.91 Å, respectively, consistent with the experimental crystal structure parameters [16]. A k-point spacing of $2\pi \times 0.04\,\text{Å}^{-1}$ was employed to generate Monkhorst-Pack k-point grids for sampling the carbon Brillouin zone. The convergence criterion were of 10^{-4} eV for total energy, and the valence electrons were treated as the C-$2s2p$, Li-$2s$, Co-$3d4s$, O-$2s2p$ electrons.

To model the positron annihilation characteristics, two-component density-functional theory (2CDFT) [17, 18] was employed to calculate the positron momentum densit. In this approach, a localized positron does not influence the average positron density. We applied the zero-positron density limits of the Boronski-Nieminen local density approximation (LDA) for the electron-positron correlation potential and enhancement factor [17]. The Doppler spectra were produced using the quantitative state-dependent model [19] and by reconstructing precise all-electron wave functions through the PAW method [19, 20]. Before comparing with experimental data, the theoretical spectra were convoluted with the experimental resolution function.

DISCUSSION

We now turn to the main results.

TABLE I. Linear Combination of DFT and EXP

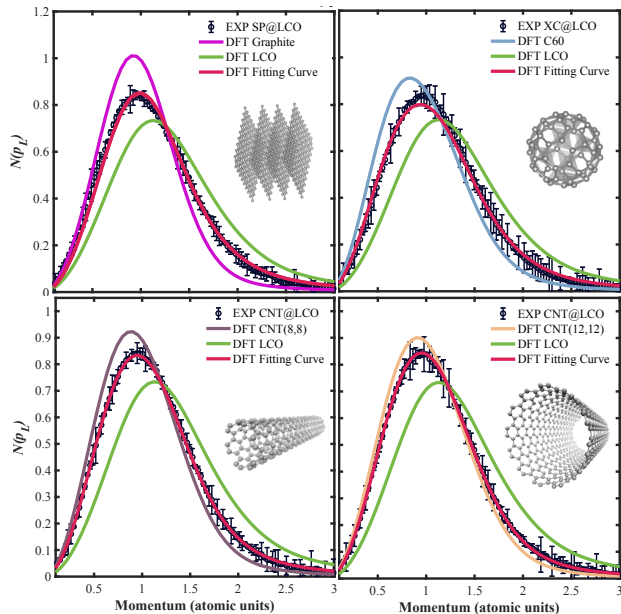| EXP	DFT	α^*	β^*	Adjusted R^2
SP	Graphite	0.496	0.504	99.731%
XC	C60	0.426	0.574	99.656%
NT	CNT 88	0.344	0.656	99.966%
	CNT 1212	0.250	0.750	99.983%

FIG. 2. Momentum distribution, N (PL) for calculated LCO and carbon, along with their linear combination, compared with experimental results from diverse samples. The momentum profiles for different sample types in (a) SP, (b) XC, and (c-d) NT, are represented by black line. The linear combination of the calculated spectra is denoted by the red solid line. These profiles are instrumental in identifying the high-momentum electron contributions, serving as a chemical fingerprint of the annihilation sites.
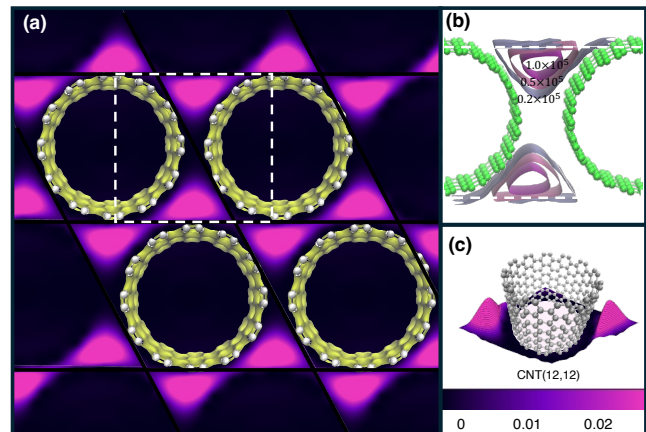

FIG. 3. (a) The positron density of CNT-12 is mapped, with areas of high density depicted in purplish-red and the electron density of the carbon nanotubes shown in yellow. (b) Within the white dashed square in (a), the positron potential energy is shown in green, and the positron wavefunctions between the nanotubes are marked on isosurfaces at 0.2×10^{-5}, 0.5×10^{-5}, and 1×10^{-5} e/Bohr^3. (c) A three-dimensional mapping of the positron density on the 001 plane.

CONCLUSION

In conclusion, our study demonstrates the power of positron annihilation spectroscopy (PAS) and coincident Doppler broadening (CDB) techniques in mapping positron momentum density and elucidating electron interactions within the cathode of lithium-ion batteries. By combining advanced two-component density functional theory (DFT) with experiments at CDB, the spatial distribution of momentum in an electron-positron annihilation environment in a carbon-coated cathode was fitted. This computational optimization model confirms that positrons can serve as amplification probes to exhibit sensitivity to π bonds in carbon-based materials, and proposes the importance of beta factors in assessing effective carbon coating. Our results highlight the potential of positron technology as an advanced tool for probing complex material systems, not only providing a new standard for material characterization in energy research, but also demonstrating sensitivity to the topology of carbon-based materials, allowing for applications in advancing superconductivity, alloy development, and other cutting-edge applications in material science.

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