Enhancing short-term electron exchange in pyrogenic carbonaceous materials through post-pyrolysis oxidative treatments

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Supplementary Information

1. Supplementary Methods

1.1 Conversion of Oxygen Content (CHN(O)S Analysis)

1. Conversion of Wt% to weight percentage (At%):

$$At\%[O] = \frac{Wt\%[O] \div MW[O]}{\sum (Wt\% \div MW)_{all}} \times 100\% \quad (1)$$

2. Conversion of Wt% to mmols/g-AC:

$$Oxygen\ Content\left(\frac{mmols}{g-AC}\right) = \frac{\frac{Wt\%[O]}{100\%}}{MW[O]} \times 1000\frac{mmols}{mole} \quad (2)$$

Wt%[O] and MW[O] represent the weight percentage and the molecular weight for oxygen as reported by CHN(O)S. $\sum (Wt\% \div MW)_{all}$ represents the sum of the Wt% divided by the molecular weight for all other elements analyzed.

2. Supplementary Tables

2.1 CHN(O)S Analysis

Table S1. CHN(O)S elemental composition (Wt-% & At-%) for X-AC, 30 min. treated H_2O_2-AC, and 30 min. treated HNO_3-AC samples. Standard deviations represent the standard error of duplicates.

	Elemental Composition									
Material	Carbon		Hydrogen		Nitrogen		Sulfur		Oxygen	
	Wt-%	At-%	Wt-%	At-%	Wt-%	At-%	Wt-%	At-%	Wt-%	At-%
X-AC	93.76 ± 0.69	92.45 ± 0.13	0.46 ± 0.01	5.40 ± 0.12	0.16 ± 0.00	0.14 ± 0.00	<0.02	<0.02	2.71 ± 0.057	2.01 ± 0.04
H2O2-AC	93.31 ± 0.90	92.45 ± 2.57	0.34 ± 0.23	4.01 ± 2.61	0.64 ± 0.56	0.54 ± 0.47	<0.02	<0.02	4.03 ± 0.46	3.00 ± 0.34
HNO3-AC	84.99 ± 1.20	83.3 ± 2.00	0.50 ± 0.04	5.83 ± 0.48	1.08 ± 0.03	0.91 ± 0.03	<0.02	<0.02	13.61 ± 1.90	10.0 ± 1.40

2.2 Density Functional Theory Analysis

Table S2. Quantitative specific surface area and pore volume data obtained for X-AC, H_2O_2-AC, and HNO_3-AC samples through DFT analysis via an Autosorb iQ system.

Sample	DFT specific surface area (m^2/g-AC)	Micropore volume (mL/g-AC)	Mesopore volume (mL/g-AC)
X-AC (30 min.)	1518.5(±10.5)	0.527(±0.005)	0.099(±0.021)
H_2O_2-AC (30 min.)	1420.8(±11.3)	0.494(±0.005)	0.083(±0.011)
H_2O_2-AC (2 min.)	1512.9(±12.9)	0.541(±0.004)	0.071(±0.002)
HNO_3-AC (30 min.)	1264.5(±10.4)	0.429(±0.003)	0.043(±0.004)
HNO_3-AC (0.5 min.)	1348.8(±9.21)	0.469(±0.003)	0.059(±0.003)

3. Supplementary Figures

3.1 Electron accepting capacities

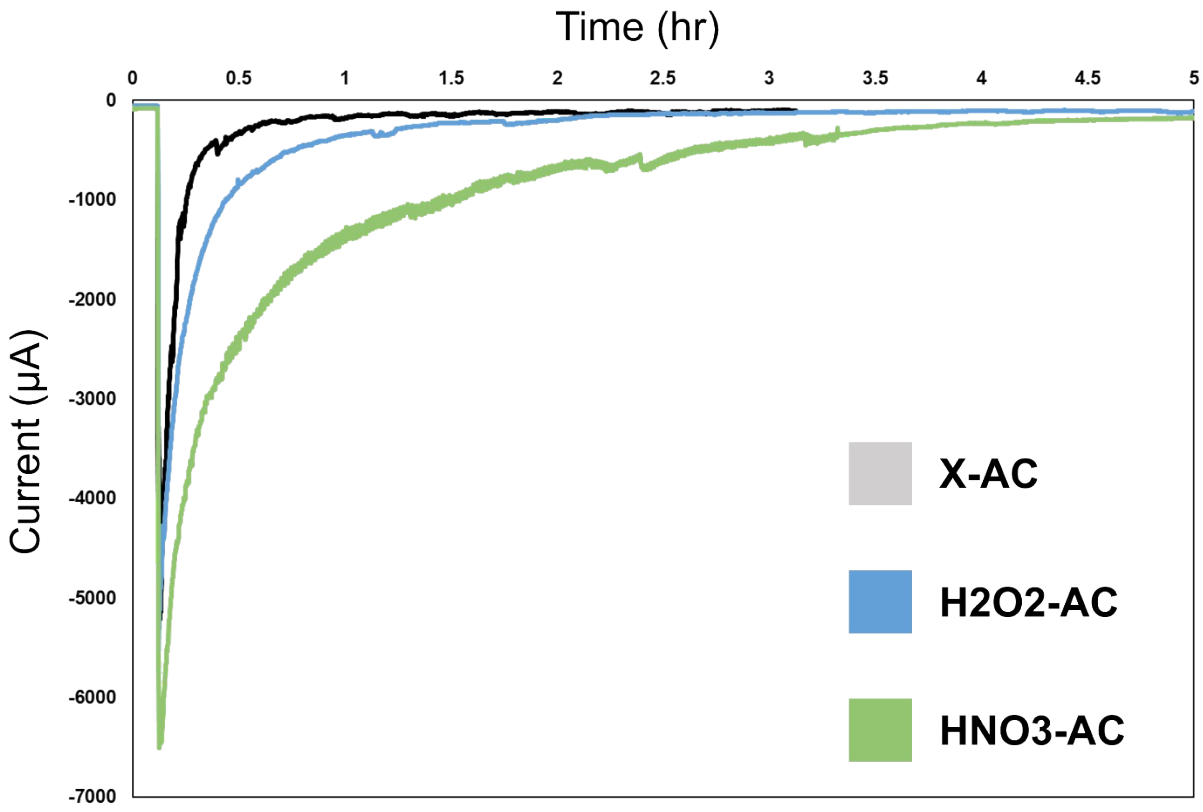

Fig. S1 Example of the current profile for X-AC, 30 min. treated H_2O_2-AC, and 30 min. treated HNO_3-AC upon injection of the sample into the electrochemical cell.

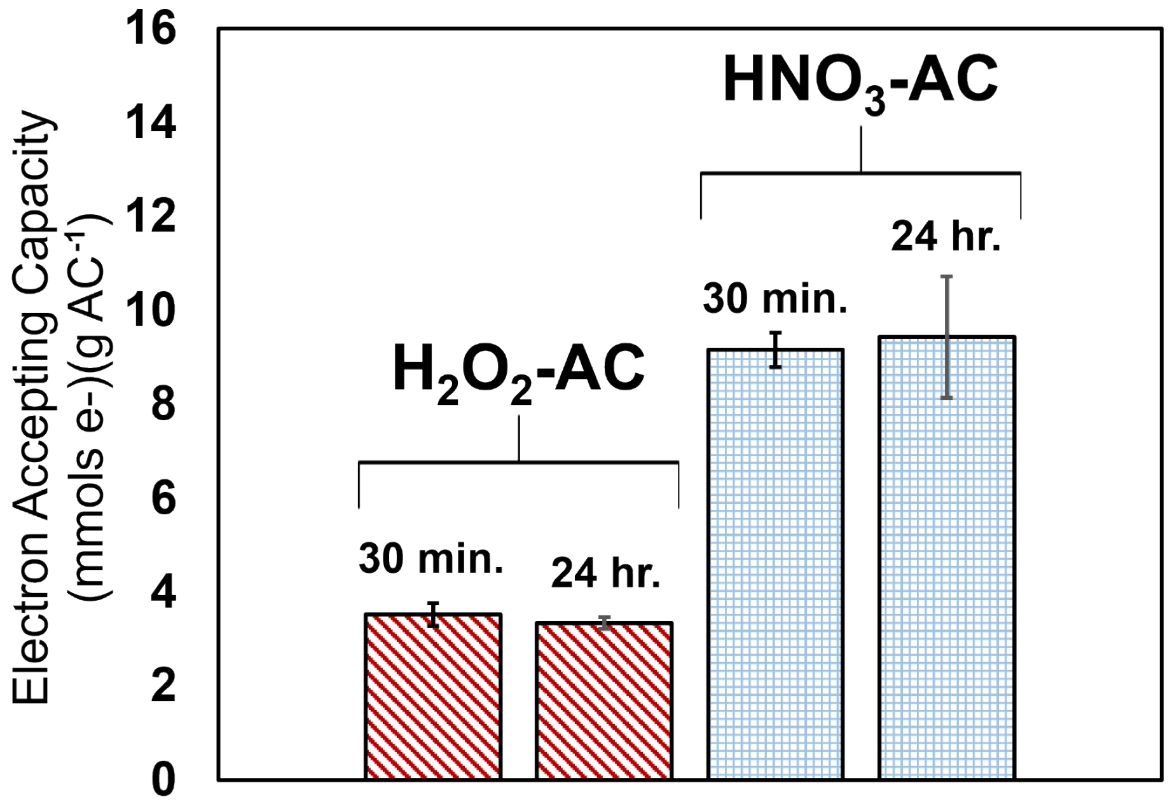

Fig. S2. Comparisons between the electron accepting capacities of H_2O_2-AC and HNO_3-AC treated for 30 minutes and 24 hours. Error bars represent the standard error of three replicates.

3.2 Electron accepting kinetics

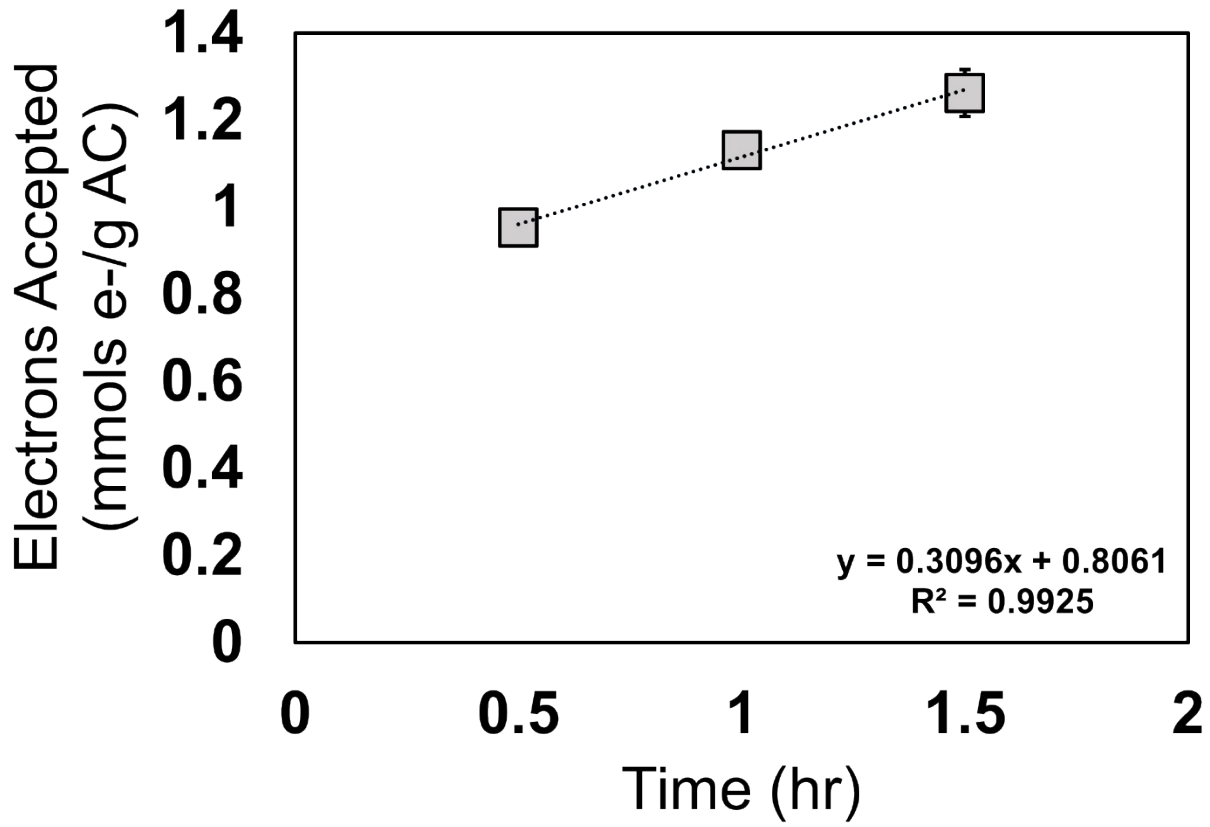

Fig. S3. Electron accepting capacity as a function of time for X-AC over the timescale of 0.5 hrs – 1.5 hrs. Error bars represent the standard error of triplicates.

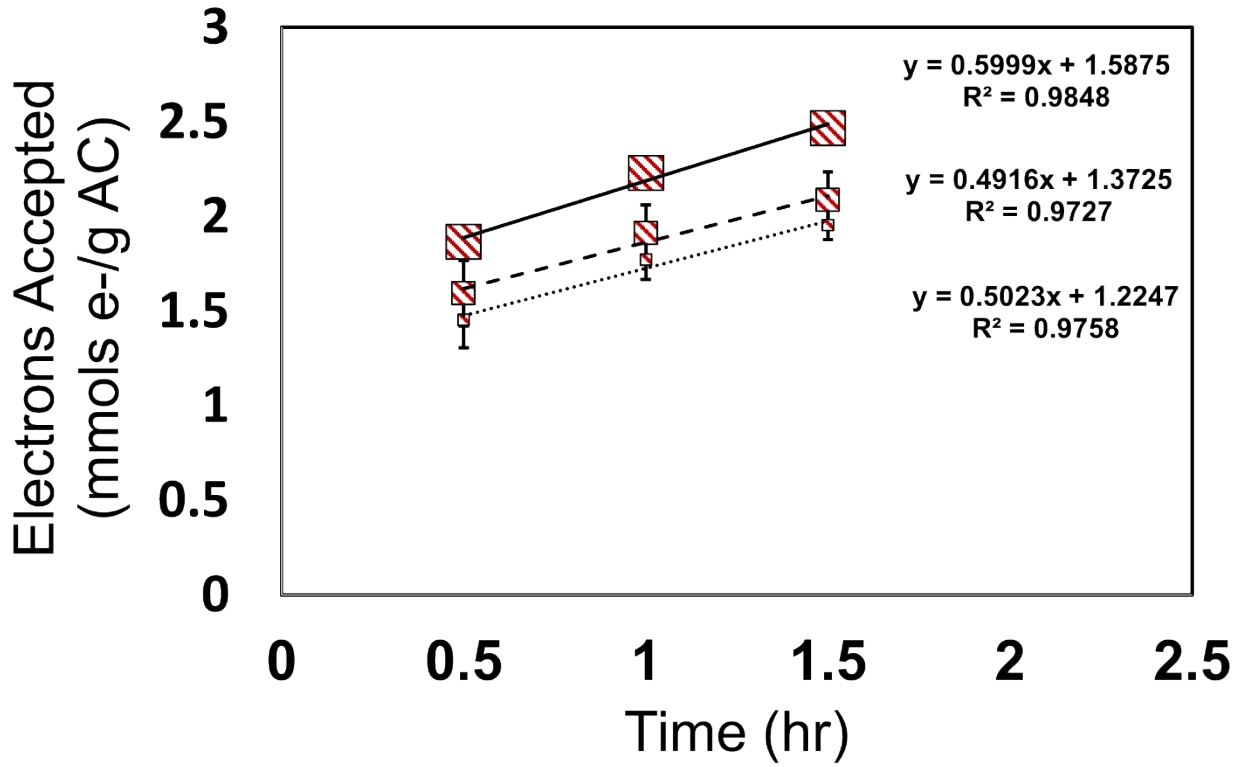

Fig. S4. Electron accepting capacity as a function of time for H_2O_2-AC samples over the timescale of 0.5 hrs – 1.5 hrs. Equations and trendlines correspond in descending order to 30 min. treated, 5 min. treated, and 2 min. treated H_2O_2-AC. Error bars represent the standard error of triplicates.

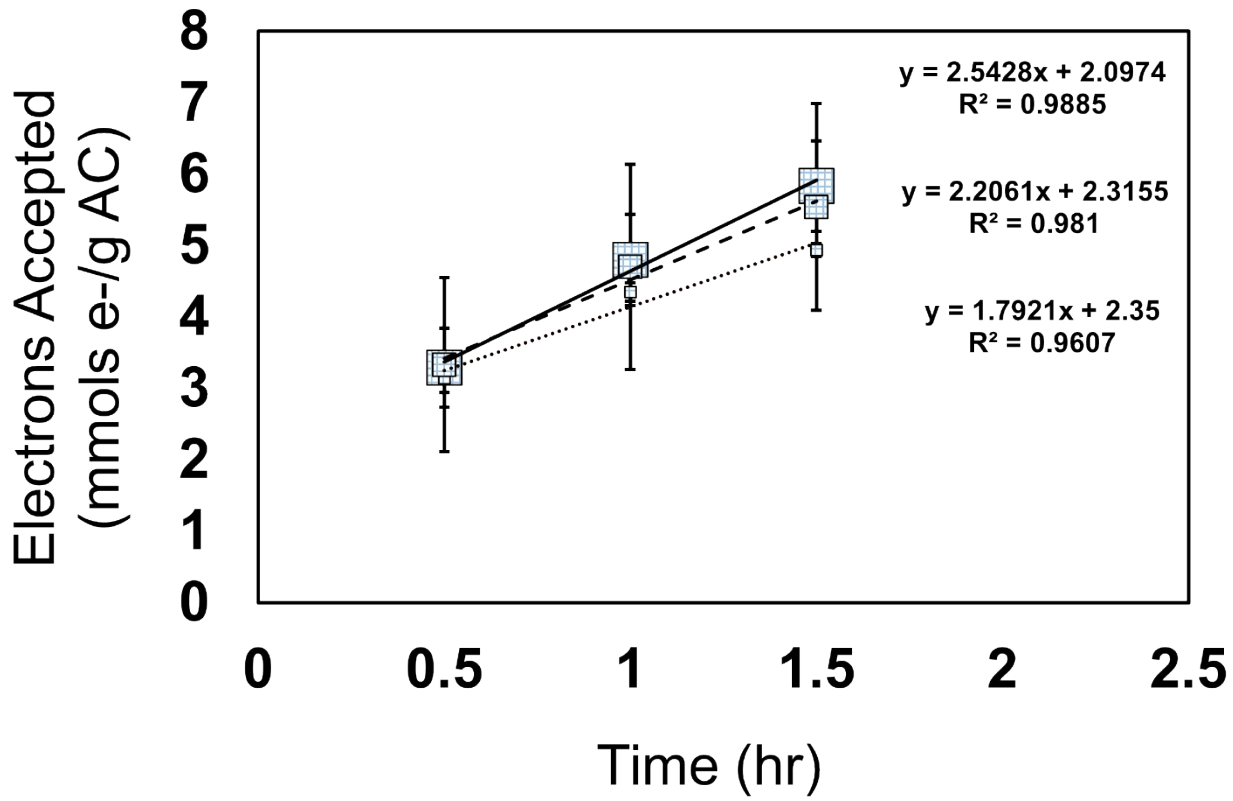

Fig. S5. Electron accepting capacity as a function of time for HNO_3-AC samples over the timescale of 0.5 hrs – 1.5 hrs. Equations and trendlines correspond in descending order to 30 min. treated, 5 min. treated, and 0.5 min. treated HNO_3-AC. Error bars represent the standard error of triplicates.

3.3 X-Ray Photoelectron Spectroscopy

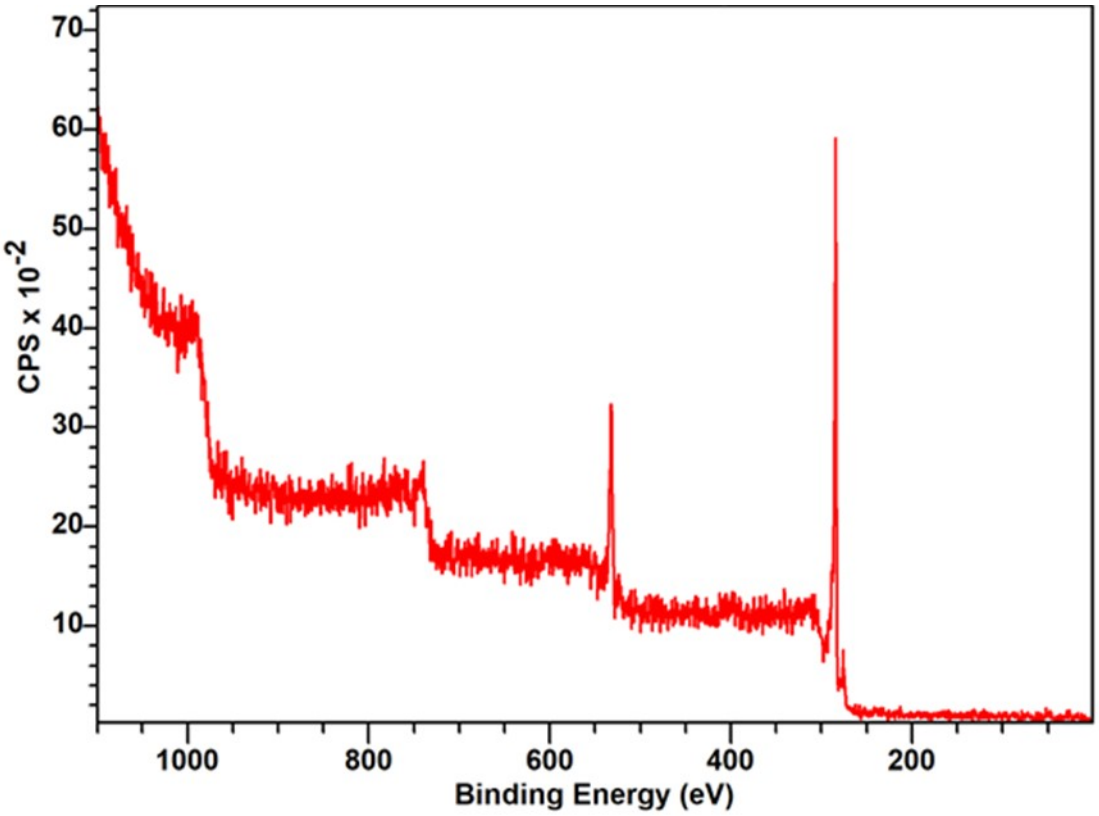

Fig. S6. Survey scan for example for a 30 minute treated HNO_3-AC sample. Survey scans for all materials corresponded to the same general structure seen here. This sample was chosen as an example since the identifiable features seen at binding energies of ~285 eV (C 1s) and ~530 eV, which were present in all samples, were most easily seen here.

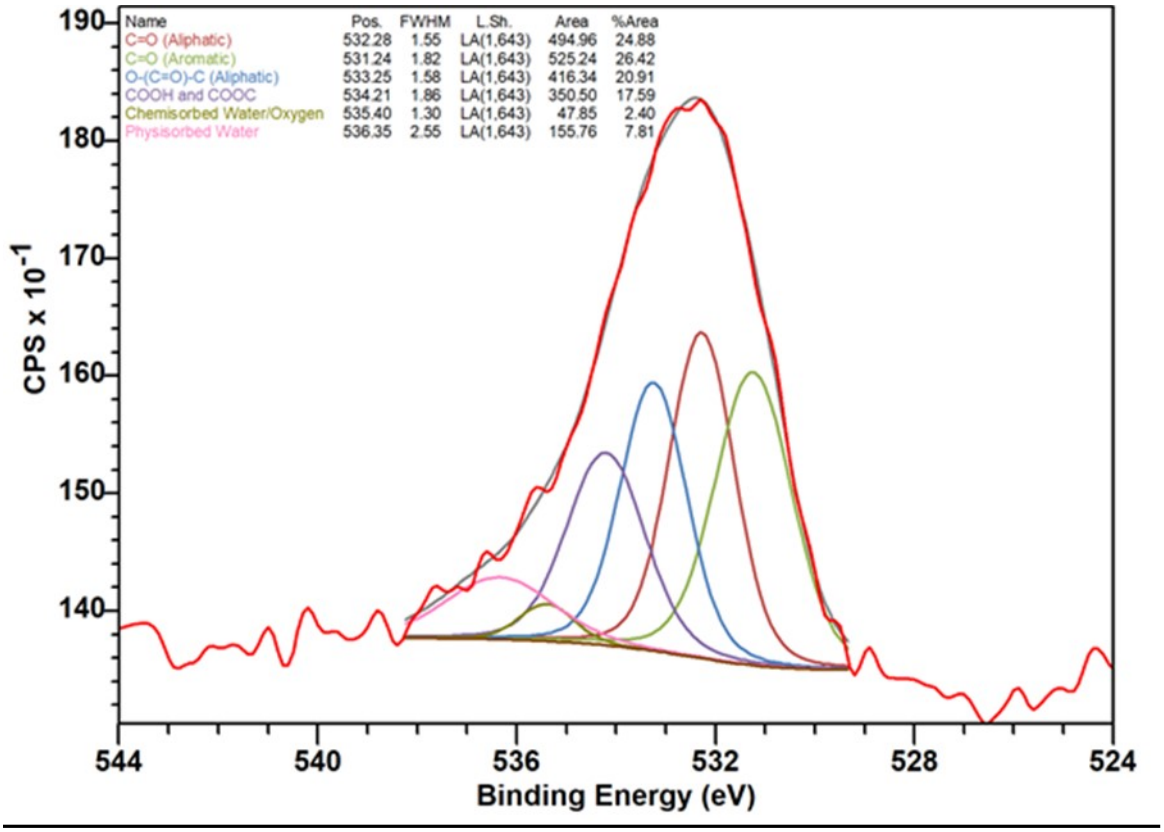

Fig. S7. Zoomed in and deconvoluted O 1s peak for a X-AC sample. Peak fitting was conducted through manual entry of individual functional groups binding energies.

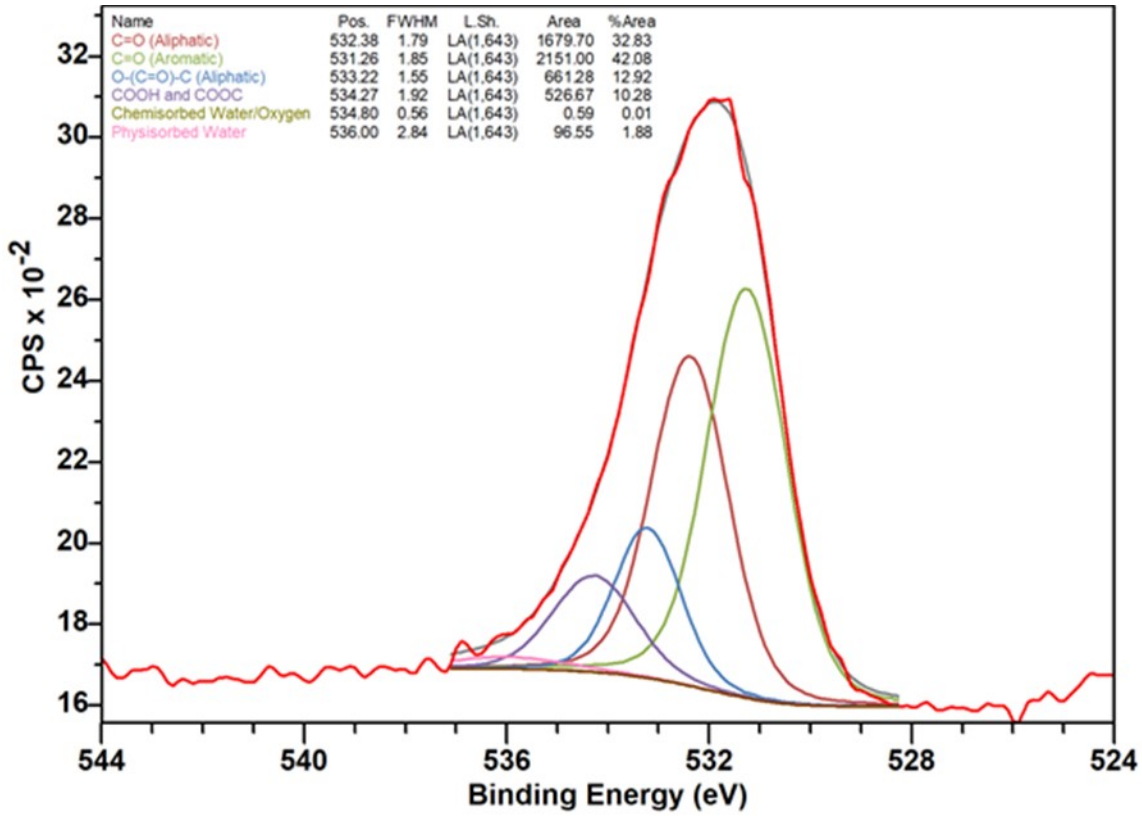

Fig. S8. Zoomed in and deconvoluted O 1s peak for an H_2O_2-AC sample. Peak fitting was conducted through manual entry of individual functional groups binding energies.

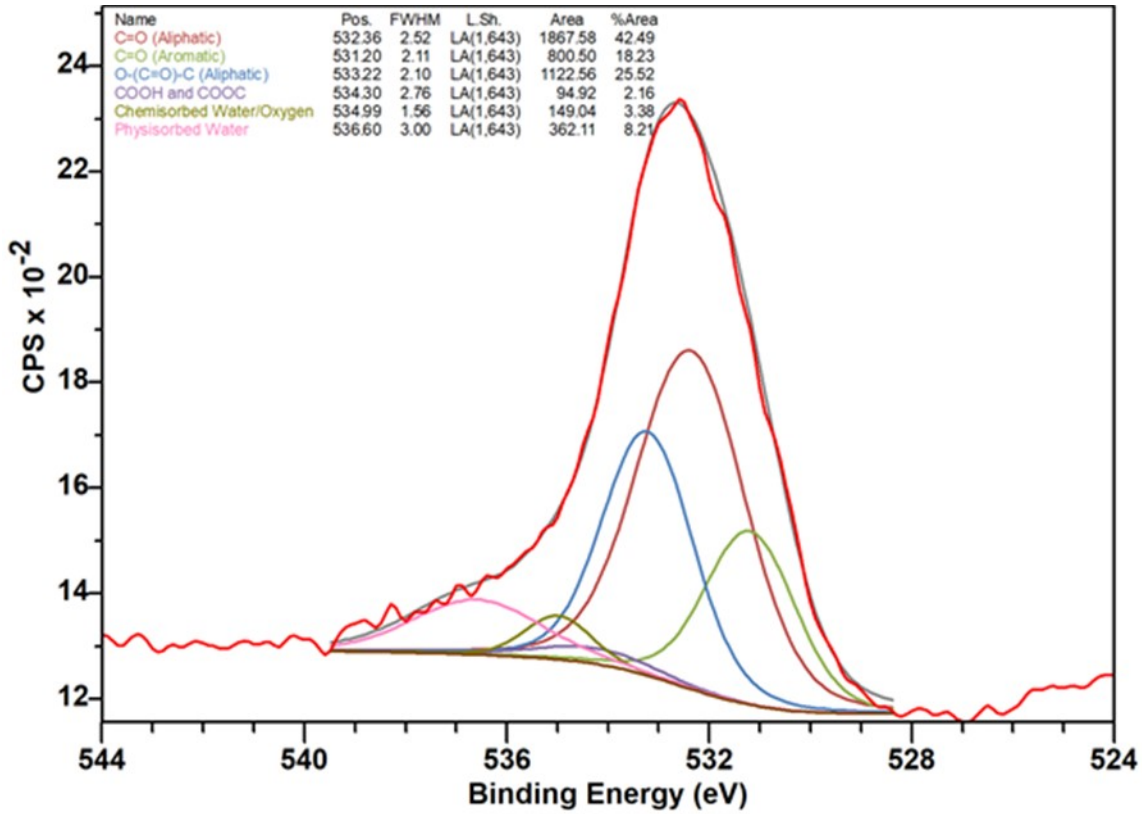

Fig. S9. Zoomed in and deconvoluted O 1s peak for an HNO_3-AC sample. Peak fitting was conducted through manual entry of individual functional groups binding energies.

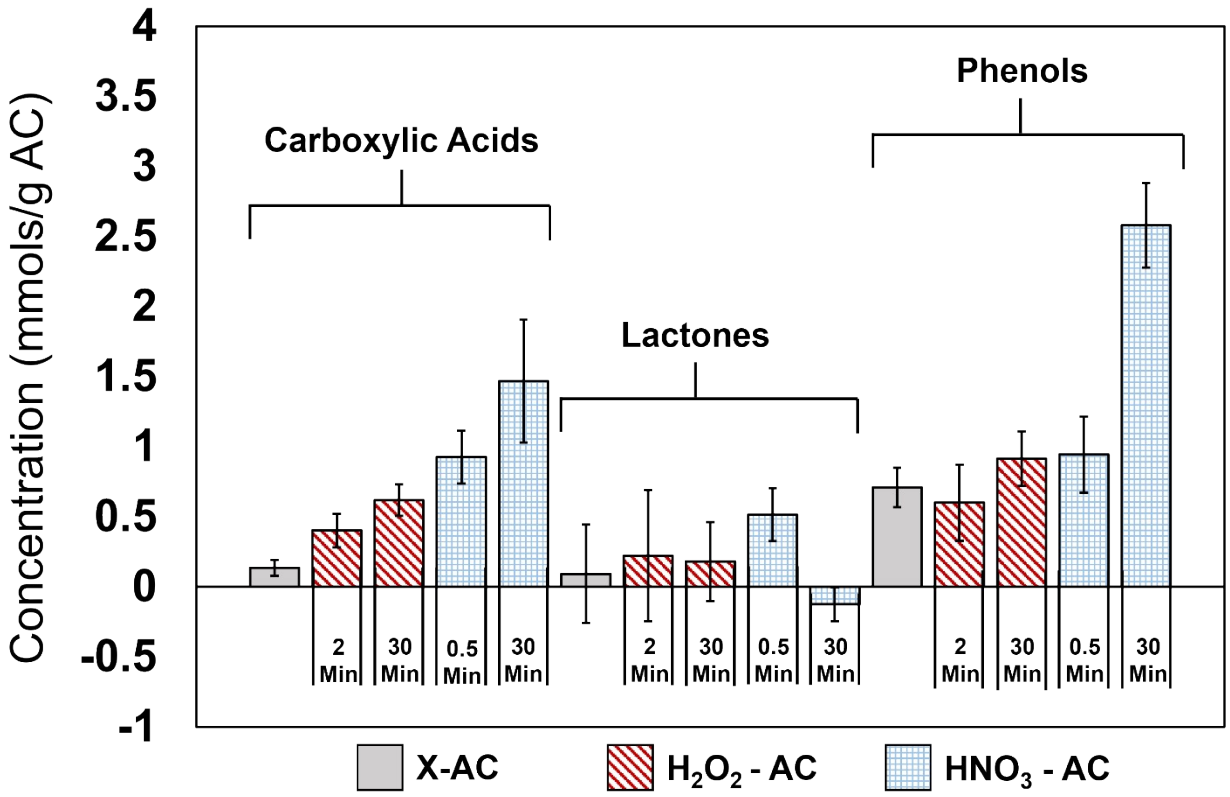

Fig. S10. Boehm titration results revealing individual functional group concentrations for X-AC, H_2O_2-AC, and HNO_3-AC. Error bars represent the standard error of triplicates.

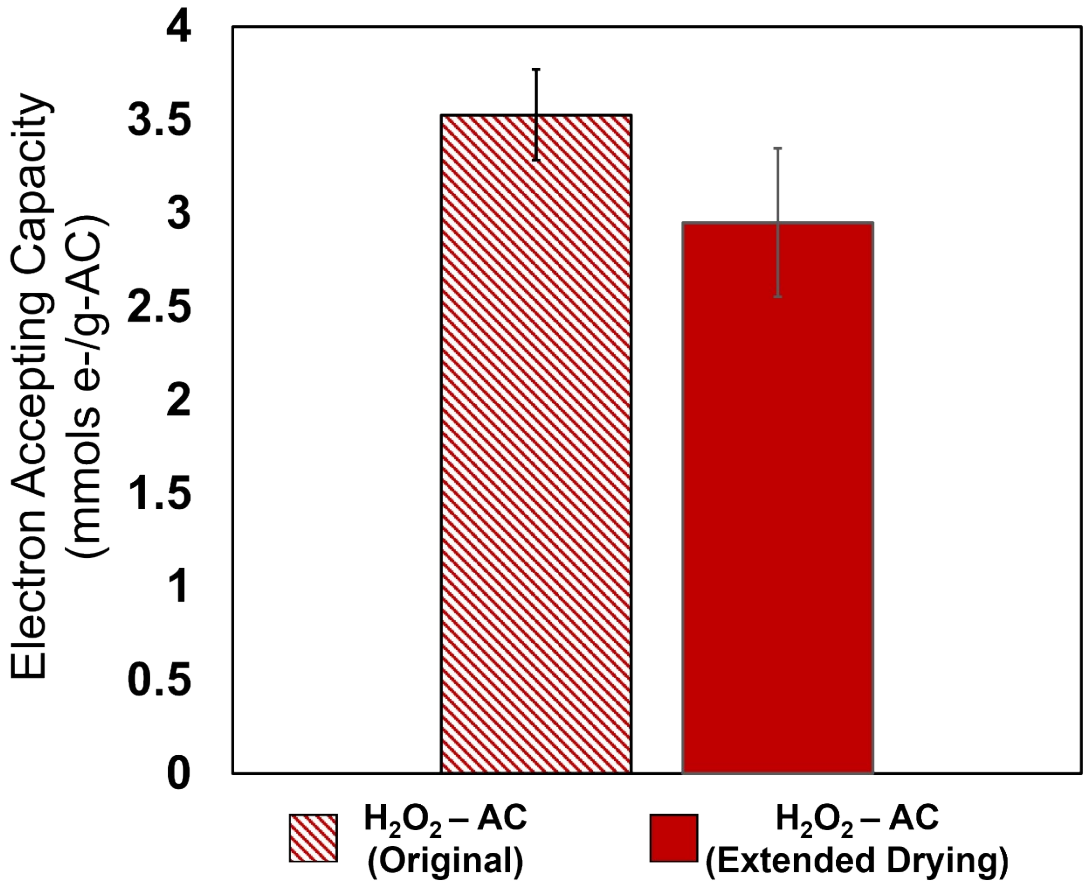

Fig. S11. EAC comparison between the 30-minute treated H_2O_2-AC sample dried at 70°C for ~30 min. and measured within 24-48 hrs and the 30-minute treated H_2O_2-AC sample dried at 105°C for ~3 hrs and measured after ~1.5 weeks. Error bars represent the standard error of triplicates.

3.3 Physical property correlation analysis

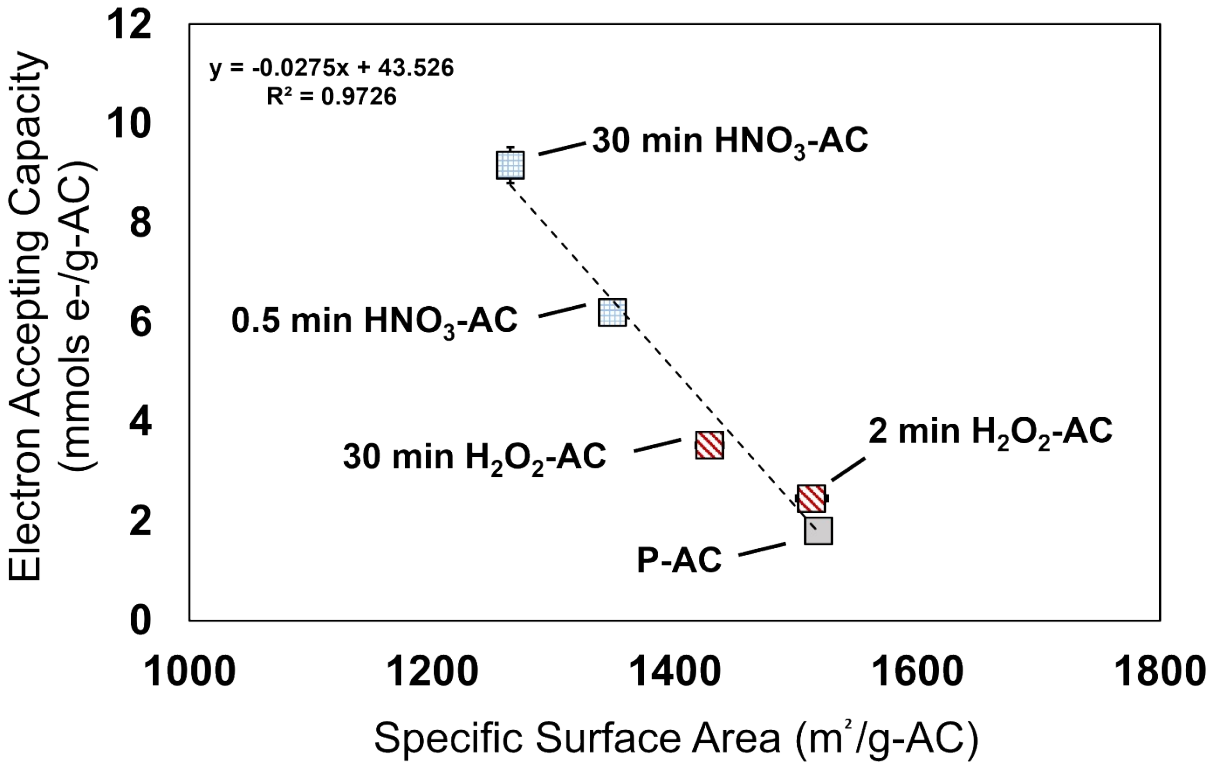

Fig. S12. Correlation plot between avg. specific surface area and avg. EAC for all untreated and treated materials. Error bars represent the standard error of three replicates.

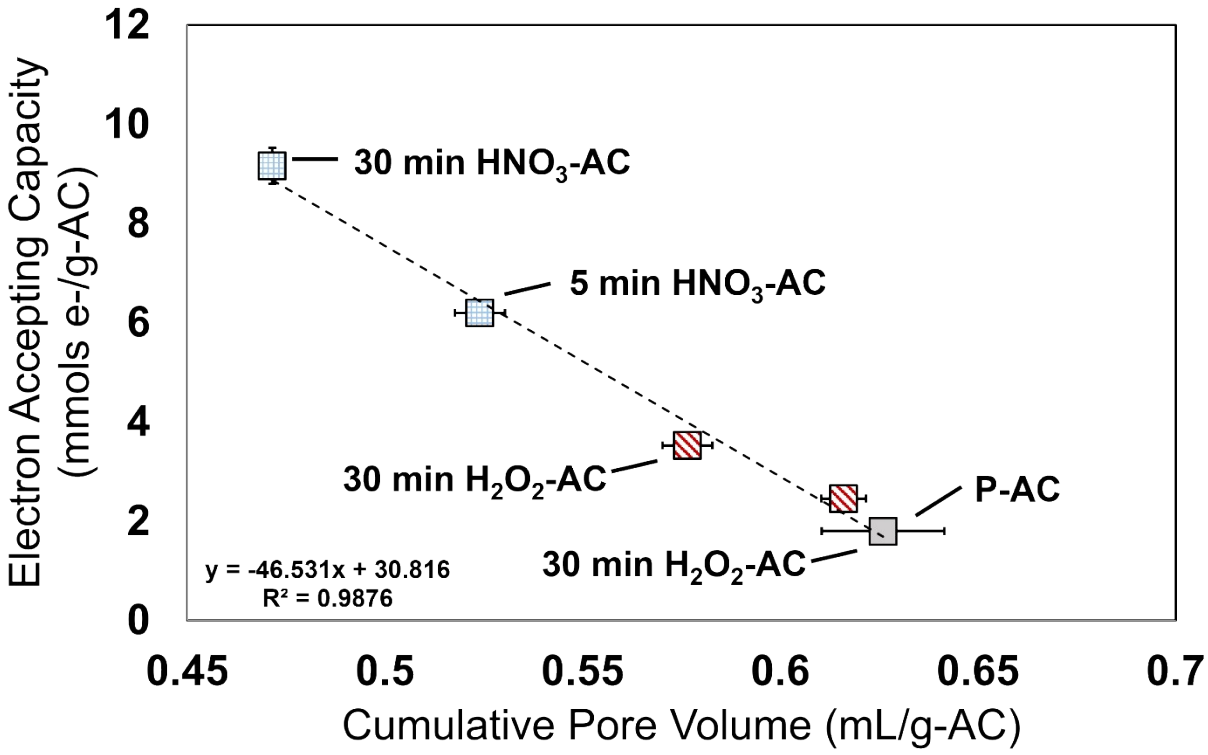

Fig. S13. Correlation plot between avg. cumulative pore volume and avg. EAC for all untreated and treated materials. Error bars represent the standard error of three replicates.