Supporting Information

Enhanced Electrochemical Performances of Li-rich Layered Oxides by Surface Modification with Reduced Graphene Oxide/$AlPO_4$ Hybrid Coating

Il Tae Kim[1], James C. Knight[2], Hugo Celio[1], and Arumugam Manthiram[1,2*]
[1]Materials Science and Engineering Program and Texas Materials Institute, [2]McKetta Department of Chemical Engineering, University of Texas at Austin, Texas 78712, United States

Determination of high-resolution C1s peaks from Casa XPS software

The entire experimental C1s envelop for each electrode consisted of three main materials: Super P, PVdF, and the SEI layer. To deconvolute the C1s envelop, the fitting parameters of the C1s peaks for PVdF and super P were determined based on the following procedure.

Using a C1s spectrum of an electrode (freshly prepared but not cycled) as a reference, the peak centers of PVdF were set at 291 eV (allowed to flow ± 0.3 eV) and 286.4 eV (fixed) while the full-width-at-half maximum (FWHM) for both peaks were set to a maximum value of 1.2 eV. The C1s peak areas of PVdF, on the other hand, were adjusted to yield a F:C ratio of 1:1. Based on this approach, the peak area of the F1s from PVdF was calculated first and then used to calculate the corresponding peak areas for peaks at 291 eV and 286.4 eV by using the relative sensitivity factors, which were assigned equal intensities because of the stoichiometry of PVdF. Subsequently, the C1s peak areas of PVdF were fixed such that they yielded the expected fluorine to carbon stoichiometric ratio for PVdF during the fitting of entire C1s envelop. For super P, the dominant peak centers were initially set to 284.6 eV, and 285 eV while the FWHM for both peaks were initially set to 0.6 and 1.2 eV, respectively. Both parameters, including their peak areas, were allowed to freely flow. The most important component of the C1s envelop of the cycled electrode is the carbonaceous species of the SEI layer. An approach adopted in this study was to choose the minimum number of SEI C1s peaks that yield the best fit between the experimental C1s envelop and the envelop fit trace, resulting in minimum noisy residuals as an indication that shows a good fit. All of the SEI parameters (peak center, FWHM, and areas) for SEI C1s at 287 and 289 eV were allowed to freely flow during the fitting of the entire C1s envelop.

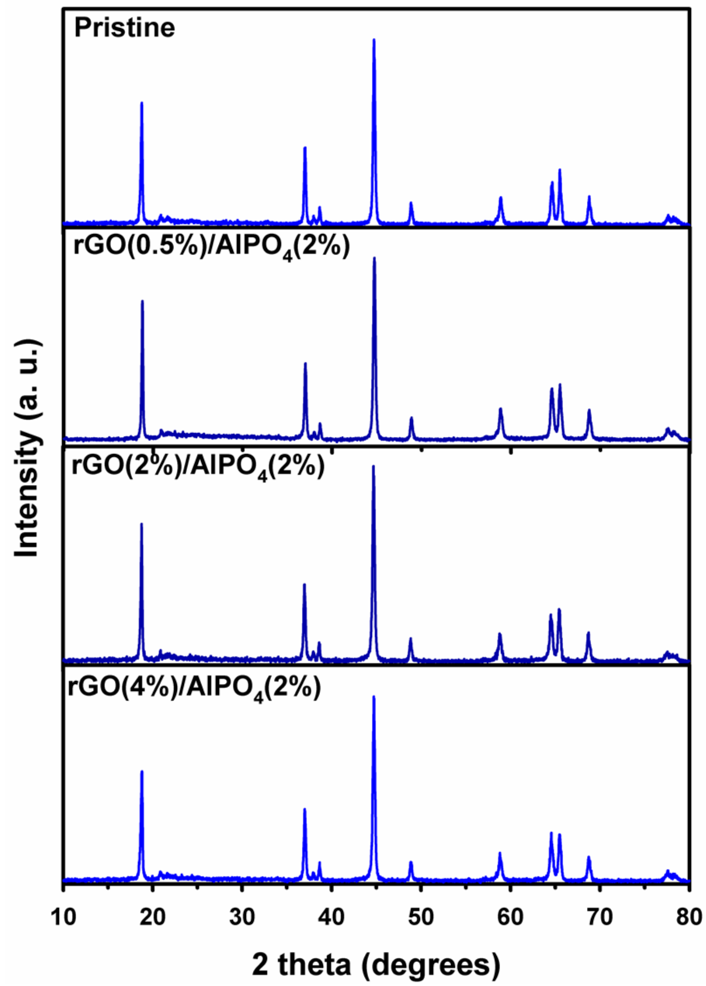

Figure S1. XRD patterns of the layered oxides before and after surface modification with various rGO/$AlPO_4$ coatings.

Characterization of the SEI layer composition as a function of time in pristine and surface-modified electrodes

Table S1 summarizes the composition of organic and inorganic species in the SEI layer and metal oxide. The compositions are normalized with respect to the manganese content. The data in Table S1 was obtained from pristine and surface-modified (rGO(0.5 wt%)/$AlPO_4$(2.0 wt%)-coated) electrodes after 50 cycles and after different elapsed times. The amount of organic and inorganic species marked with red underlines in Table S1 decreased with increasing rest time, illustrating an unstable SEI layer. Therefore, it is very important to set a strict testing protocol to obtain reliable experimental results.

Furthermore, when investigating the lithium content, the pristine electrode reveals an increase in lithium content while the surface-modified electrode shows a slight decrease in lithium content after an extended rest time. This could be attributed to the existence of more lithium in the pristine electrode's SEI layer, which affects the overall electrochemical properties as discussed in the manuscript. The rGO(1.0 wt%)/$AlPO_4$(2.0 wt%)-coated electrode also shows the same tendency as the rGO(0.5 wt%)/$AlPO_4$(2.0 wt%)-coated electrode.

Table S1. Composition analysis of (a) pristine and (b) surface modified (rGO(0.5wt%)/$AlPO_4$(2.0wt%)-coated) electrodes after 50 cycles by XPS

(a)

hrs. under UHV	48.00				66				90				114				Ratio Difference (114hrs-48hrs)
region (description)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	
C 1s (super P)	284.6	0.6	8.00	10.53	284.6	0.6	10.35	13.99	284.6	0.6	11.58	14.30	284.6	0.6	11.84	13.01	2.48
C 1s (-CC)	284.9	1.5	16.50	21.71	285.1	1.7	17.78	24.03	285.2	1.8	22.93	28.31	285.2	1.8	24.37	26.78	5.07
C 1s (-CO2)	287.3	1.8	10.17	13.38	287.3	1.9	9.28	12.54	287.5	1.9	7.53	9.30	287.5	1.9	7.06	7.76	-5.62
C 1s (PVdF)	291.0	1.2	6.76	8.89	290.9	1.3	5.93	8.01	290.7	1.4	4.61	5.69	290.7	1.4	4.34	4.77	-4.13
C 1s (CO3)	289.4	1.5	1.94	2.55	289.2	1.5	1.67	2.26	289.2	1.6	1.43	1.77	289.0	1.5	1.16	1.27	-1.28
C 1s (PVdf)	286.4	1.4	7.56	9.95	286.4	1.4	5.93	8.01	286.4	1.4	4.61	5.69	286.4	1.4	4.36	4.79	-5.16
O 1s	533.9	1.9	6.24	8.21	533.9	2.0	5.61	7.58	533.6	2.1	5.02	6.20	533.5	2.1	4.70	5.16	-3.05
O 1s	532.4	1.7	9.10	11.97	532.4	1.8	9.02	12.19	532.2	1.8	8.72	10.77	532.1	1.8	8.79	9.66	-2.31
O 1s (O-metal)	529.8	1.2	1.26	1.66	529.8	1.2	1.38	1.86	529.8	1.2	1.50	1.85	529.7	1.2	1.46	1.60	-0.05
F 1s (PVdF)	687.8	1.9	13.87	18.25	687.7	2.0	13.48	18.22	687.6	2.1	11.96	14.77	687.5	2.1	11.41	12.54	-5.71
F 1s	685.5	2.0	3.45	4.54	685.3	1.7	2.75	3.72	685.2	1.7	2.73	3.37	685.1	1.6	2.51	2.76	-1.78
P 2p	134.7	2.0	1.19	1.57	134.7	2.2	1.26	1.70	134.1	1.6	0.73	0.90	134.4	2.0	1.33	1.46	-0.10
P 2p	136.5	2.1	0.67	0.88	136.4	2.1	0.48	0.65	135.4	2.1	0.95	1.17	136.0	2.0	0.36	0.40	-0.49
Li 1s	56.0	2.4	12.53	16.49	55.8	2.4	14.32	19.35	55.8	2.4	14.90	18.40	55.6	2.5	15.58	17.12	0.63
Mn 2p	642.3	4.2	0.76	1.00	642.3	3.7	0.74	1.00	642.3	3.8	0.81	1.00	642.1	3.6	0.91	1.00	0.00

(b)

hrs. under UHV	48.00				66				90				114				Ratio Difference (114hrs-48hrs)
region (description)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	Position (eV)	FWHM (eV)	%At. Conc.	ratio (X/Mn)	
C 1s (super P)	284.5	0.6	4.07	4.96	284.6	0.6	4.85	5.51	284.5	0.6	5.90	6.48	284.5	0.6	6.05	6.37	1.41
C 1s (-CC)	285.3	1.8	20.40	24.88	285.5	1.9	23.23	26.40	285.4	1.8	28.01	30.78	285.3	1.8	27.72	29.18	4.30
C 1s (-CO2)	287.2	1.6	14.61	17.82	287.5	1.8	12.58	14.30	287.3	1.8	10.26	11.27	287.1	2.3	13.76	14.48	-3.33
C 1s (PVdF)	291.1	1.1	3.73	4.55	291.1	1.4	3.88	4.41	290.8	1.7	3.49	3.84	290.9	1.4	2.16	2.27	-2.28
C 1s (CO3)	289.5	1.9	7.34	8.95	289.6	1.7	5.83	6.63	289.2	1.8	5.04	5.54	289.5	1.8	4.39	4.62	-4.33
C 1s (PVdf)	286.4	1.6	3.73	4.55	286.7	1.6	3.85	4.38	286.7	1.6	3.50	3.85	286.9	1.6	2.18	2.29	-2.25
O 1s	534.0	1.7	8.61	10.50	534.1	1.8	7.47	8.49	533.9	1.9	6.53	7.18	533.9	1.9	5.64	5.94	-4.56
O 1s	532.5	2.0	12.46	15.20	532.5	2.1	12.46	14.16	532.3	2.0	11.70	12.86	532.3	2.1	12.20	12.84	-2.35
O 1s (O-metal)	529.8	1.3	1.50	1.83	529.8	1.2	1.60	1.82	529.8	1.2	1.70	1.87	529.7	1.2	1.74	1.83	0.00
F 1s (PVdF)	688.0	1.9	6.74	8.22	687.9	2.1	7.99	9.08	687.7	2.1	7.58	8.33	687.7	2.2	7.95	8.37	0.15
F 1s	686.1	2.4	6.70	8.17	685.9	2.3	5.91	6.72	685.8	2.2	5.17	5.68	685.7	2.1	4.89	5.15	-3.02
P 2p	134.5	2.0	0.89	1.09	134.5	2.2	0.99	1.13	134.2	1.7	0.64	0.70	134.4	2.0	1.10	1.16	0.07
P 2p	136.2	2.4	0.88	1.07	136.0	2.7	0.90	1.02	135.4	2.8	1.27	1.40	135.7	2.8	0.82	0.86	-0.21
Li 1s	55.8	2.0	6.72	8.20	55.8	2.4	6.82	7.75	55.9	2.3	7.49	8.23	55.7	2.3	7.47	7.86	-0.33
Al 2p	75.5	2.1	0.79	0.96	75.5	1.9	0.76	0.86	75.4	2.0	0.82	0.90	75.4	2.2	0.99	1.04	0.08
Mn 2p	642.4	3.7	0.82	1.00	642.4	3.5	0.88	1.00	642.3	3.5	0.91	1.00	642.3	3.5	0.95	1.00	0.00