Increased demand for reliable high power energy storage devices has led to growing interest in the development of novel electrode materials for electrochemical capacitors (ECs). One of the most promising approaches in EC electrode design involves the fabrication of nanostructured composites in which pseudocapacitive materials are immobilized on electrochemical double layer capacitive (EDLC) carbon substrates. There is synergy in this combination as the pseudocapacitive material allows for large charge storage capacity due to surface redox reactions, while the carbon substrate imparts mechanical stability, improved conductivity, and physical capacitive effects. These types of composite materials including RuO₂-CNT, MnO₂-graphene, V₂O₅-CNT, and conductive organic polymer (COP)-CNT have been investigated extensively for pseudocapacitive EC electrodes.

Although there are many pseudocapacitive alternatives, polyoxometalates (POMs), nanoscale transition metal-oxygen clusters, have emerged as promising building blocks for nanocomposite electrodes. POMs have an unmatched range of physical and chemical properties which arise from their seemingly endless variety of molecular structures and sizes. One of the most common and widely researched classes of POM molecules is the Keggin cluster which has the general formula [MX₁₂O₄₀ⁿ⁻] in which the central heteroatom (i.e., P, Si, or Ge) is surrounded by twelve addenda atoms (i.e., Mo or W) and forty oxygen atoms. These molecules demonstrate high stability of their redox states and participate in fast reversible multi-electron transfer reactions, making them ideally suited for pseudocapacitive applications. They also offer tremendous versatility as their electrochemical behavior can be tuned with small adjustments to the molecular chemistry.

The electrochemical activity of POMs can be combined with the stability and high surface area of carbon substrates to create robust nanocomposite EC electrodes. These POM-carbon composites can be prepared by a variety of techniques including electrodeposition, chemisorption, and layer-by-layer (LbL) self assembly. The improved capacitive properties of MWCNT electrodes modified with PMO₁₂O₄₀³⁻ (PMO₁₂) through chemisorption have been well documented. Furthermore, Gomez-Romero has shown that POMs can be effectively immobilized on activated carbon electrodes to achieve enhanced capacitance as well as dramatic improvements in power density. Most recently, reports of high performance graphene-POM nanocomposite EC electrodes have also emerged.

These studies demonstrate the potential for POMs as effective pseudocapacitive materials; however, these studies only explored a few commercially available POM chemistries like PMO₁₂ or PW₁₂O₄₀³⁻ (PW₁₂). There are hundreds of POM molecules, each with unique properties that have yet to be explored for EC applications. Investigating a wide range of these molecules is very important, as the use of individual POM chemistries presents challenges for EC applications. The cyclic voltammograms (CVs) of Keggin POMs like PMO₁₂ or PW₁₂ do not show the ideal rectangular profile that the LbL technique can be used to superimpose different POM molecules on the same electrode. With this method, multiple POM chemistries with different redox peak potentials can be combined to achieve overlapping redox features and a more ideally capacitive CV profile.

In addition to the multi-layer technique, a mixed layer coating approach can also be used to combine the effects of multiple POMs. For this method, different POM molecules are combined in an aqueous solution and coated on the electrode simultaneously in a single active layer. This simple process minimizes the electrochemically inert polymer layers and in certain cases, POM mixtures have been shown to result in synergistic combinations. For instance, when PMO₁₂ and PW₁₂ are combined in a mixed layer electrode, the resulting composite does not display a simple combination of PMO₁₂ and PW₁₂ redox behavior, but instead exhibits its own unique electrochemical activity. This interesting electrochemical phenomenon was reported in our recent communication, however, the underlying cause of this behavior was not well understood. In this study, we expand upon this work to gain a better understanding of how these molecules interact in the mixture and how these interactions affect the electrochemical properties of the composite electrode. We will also demonstrate how these POM mixtures can be used in conjunction with multi-layer modification to design molecular coatings that overcome the limitations of individual POM chemistries to achieve enhanced charge storage and a more ideally capacitive CV profile.
Experimental

**POM synthesis.** — H₂PMo₁₂O₄₀ (PMo₁₂), H₂PW₁₂O₄₀ (PW₁₂), H₂SiMo₁₂O₄₀ (SiMo₁₂) were all purchased from Alfa Aesar, while H₂GeMo₁₂O₄₀ (GeMo₁₂) was synthesized according to a previously described method.²⁶ The mixed addenda H₁₂PMo₆W₁₄O₄₆ (PMo₆W₄) was prepared by the conventional etherate method. Briefly, 15.0 g NaMoO₄·2H₂O, 6.82 g Na₃WO₄·2H₂O, and 1.85 g Na₂HPO₄·2H₂O were dissolved in deionized water and the pH was adjusted to 1.5 with H₂SO₄. The mixture was stirred continuously for 4 hours at 80°C. The cooled solution was extracted with ether and the isolated solid was washed with deionized water and dried for 5 hours at 50°C yielding a yellow crystal product. All reagents for the synthesis were purchased from Alfa Aesar.

**Electrode fabrication: layer-by-layer (LbL) process.** — MWCNT electrode films were fabricated by combining the “as-received” MWCNTs with 4 wt% PTFE binder and rolling into thin films of approximately 100 μm thickness. The POMs were dissolved in deionized water to form 10 mM coating solutions. The mixed coating solutions were also prepared on a 10 mM basis (i.e., the 3:1 PMo₁₂−PW₁₂ mixture was 7.5 mM PMo₁₂ and 2.5 mM PW₁₂). The LbL process used to fabricate the composite MWCNT-POM electrodes proceeded according to the following steps:

1. Soaking of the MWCNT film in concentrated HNO₃ (2 minutes) followed by H₂O washing (2 minutes)
2. Soaking in 4 wt% poly(diallyldimethylammonium chloride) (PDDA) solution (10 minutes) followed by H₂O washing (2 minutes)
3. Soaking in POM solution (20 minutes) followed by H₂O washing (2 minutes)

Characterizations. — Electrochemical Analysis was performed on the bare and composite MWCNT films in a 3-electrode system. A cavity microelectrode (CME) was used as the working electrode, the bare and composite MWCNT films in a 3-electrode system. A pure PMo₁₂-modified, and pure PW₁₂-modified MWCNT for comparison. The cyclic voltammogram of a CNT electrode modified with an equimolar mixture of PMo₁₂ and PW₁₂ is shown in Figure 1 along with the profiles for bare, pure PMo₁₂-modified, and pure PW₁₂-modified MWCNT for comparison. When two polyanionomtate molecules are combined equally in a mixed active layer, one could reasonably expect the resulting CV profile to be an equally weighted combination of the pure component CVs. A 50-50 weighted combination of the pure PMo₁₂ and PW₁₂ CV curves was calculated and plotted (gray line) as a prediction of the mixed layer CV shape.

Results and Discussion

**Polyoxometalate mixtures.** — Electrochemical behavior. — We have explored the electrochemical properties of MWCNT electrodes modified with a mixed polyanionomtate active layer combining molybdenum-containing PMo₁₂ with tungsten-containing PW₁₂. The cyclic voltammogram of a CNT electrode modified with an equimolar mixture of PMo₁₂ and PW₁₂ is shown in Figure 1 along with the profiles for bare, pure PMo₁₂-modified, and pure PW₁₂-modified MWCNT for comparison. When two polyanionomtate molecules are combined equally in a mixed active layer, one could reasonably expect the resulting CV profile to be an equally weighted combination of the pure component CVs. A 50-50 weighted combination of the pure PMo₁₂ and PW₁₂ CV curves was calculated and plotted (gray line) along with the experimental data in Figure 1. With this simple model as a reference, it is clear that the actual CV of the PMo₁₂-PW₁₂ mixture (red line) does not resemble an equal combination of the pure PMo₁₂ and PW₁₂ profiles. This was somewhat surprising, as X-Ray Photoelectron Spectroscopy (XPS) confirmed that Mo and W were deposited on the electrode surface in an equal molar ratio.²⁷ Nonetheless, the mixed active layer appears to have its own characteristic electrochemical activity. When compared to the model combination, the actual mixed layer CV displays much broader redox waves occurring at different redox peak potentials. This behavior suggests that an effect beyond simple mixing is at play when PMo₁₂ and PW₁₂ are combined.

To better understand the reason for this mixture phenomena and how to leverage it for pseudocapacitive applications, a series of mixed active layer electrodes with varying ratios of PW₁₂ to PMo₁₂ were evaluated. The composition of each mixed layer electrode and their redox peak potentials are summarized in Table I with the cyclic voltammograms shown in Figure 2. The CV of the pure PMo₁₂ layer displayed three reversible redox peaks (labelled I, II, and III in Figure 2), each corresponding to the characteristic 2 electron transfer processes of the PMo₁₂ molecule.²⁵ When PW₁₂ is introduced to the active layer incrementally, a consistent trend appears in the CV profiles; the redox peak current densities all decrease while the peak widths broaden significantly. This broadening of the redox waves becomes more dramatic at higher PW₁₂ concentrations (above 37.5%) as the first redox peak develops a shoulder at higher potentials and the second and third redox waves begin to merge together. Even more interesting is that while the potential of the first redox peak remains relatively constant for all mixtures, the second and third redox peaks shift consistently to lower potentials in a manner proportional to the amount of PW₁₂ introduced to the mixture. In fact, when the second and third redox peaks shift to lower potentials in a manner proportional to the amount of PW₁₂ introduced to the mixture. In fact, when the second and third redox peaks shift to lower potentials in a manner proportional to the amount of PW₁₂ introduced to the mixture.
It is clear from these results that none of the mixed active layers display a weighted combination of pure PMo12 and PW12 redox features. Rather, each mixture has its own characteristic electrochemical behavior, similar to that of PMo12, but with much broader redox waves shifted to lower peak potentials. These dramatic changes in electrochemical properties suggest that when PW12 is added to the coating solution, it does not just mix with PMo12 molecules, but instead promotes a chemical change. The electrochemical activity of the Keggin molecule is very sensitive to the addenda atom chemistry; the oxidation and reduction of these addenda atoms is what produces the Keggin redox features. The redox potential of the tungsten atom is much lower than that of molybdenum. Thus, the highly proportional negative shift in the redox peak potentials of the mixture with added PW12 suggests that the change promoted by the PW12 addition may affect the addenda stoichiometry of the Keggin cluster.

**Structural analysis.—** X-Ray Diffraction (XRD) was conducted on the PMo12-PW12 mixtures to investigate potential structural changes that result from the combination of these molecules in solution. An equimolar aqueous mixture of PMo12-PW12 (the same type used for the LbL deposition process) was prepared and dried at 70°C for 8 hours to recover the solid powder. The XRD pattern of this solution-prepared solid mixture was compared to that of a physical (dry) mixture of the dry mixture shows two small features at 2θ = 207.24° and 2θ = 231.80° which are commonly reported features. Rather, each mixture has its own characteristic electrochemical behavior, similar to that of PMo12, but with much broader redox waves shifted to lower peak potentials. These dramatic changes in electrochemical properties suggest that when PW12 is added to the coating solution, it does not just mix with PMo12 molecules, but instead promotes a chemical change. The electrochemical activity of the Keggin molecule is very sensitive to the addenda atom chemistry; the oxidation and reduction of these addenda atoms is what produces the Keggin redox features. The redox potential of the tungsten atom is much lower than that of molybdenum. Thus, the highly proportional negative shift in the redox peak potentials of the mixture with added PW12 suggests that the change promoted by the PW12 addition may affect the addenda stoichiometry of the Keggin cluster.

**Mixed addenda synthesis and comparison.—** If the PMo12-PW12 solution mixture indeed results in a chemical change while still retaining the Keggin structure, the most likely explanation is the formation of a mixed addenda POM molecule. In this scenario, illustrated in Figure 4A, the combination of PMo12 and PW12 clusters in solution promotes the rearrangement of the constituent elements as a mixed addenda Keggin species combining both tungsten and molybdenum addenda atoms on the same molecule. This process is very sensitive to the stoichiometry of the mixture as the molar ratio of PMo12 to PW12 in solution will determine the addenda atom composition of the product molecule. For instance, a solution combining PMo12 and PW12 in a 3:1 molar ratio would result in the synthesis of PMo9W3O403 which has a 3:1 ratio of Mo to W addenda atoms. This would explain why the molar ratio of PW12 in the coating solution has such a consistent and dramatic effect on the electrochemical behavior of the mixed coating layer.

In order to confirm the proposed mixed addenda synthesis described above, the electrochemical behavior of a 3:1 molar mixture of PMo12 and PW12 was compared to that of PMo9W3O403 (PMo9W3) species synthesized by the conventional ethereate method. Figure 4B shows the CV of the 3:1 PMo12-PW12 mixed layer-modified MWCNT electrode compared with that of the PMo9W3-modified electrode. The CV profile of the mixture is almost identical to that of the synthesized mixed addenda species, with both showing three sets of redox waves with very identical peak current densities and potentials. It should be noted that POM molecules especially mixed addenda species, display a complex equilibrium in aqueous solutions. Thus, even when using the conventional ethereate synthesis method, the product may not be pure PMo9W3, but rather a complex mixture of different mixed addenda species. Nevertheless, the comparison in Figure 4B shows that the simple mixing approach yields the same complex mixture as the conventional mixed-addenda POM synthesis method. These are not just random mixtures; increasing the proportion of tungsten in the PMo12-PW12 solution caused a consistent and proportional decrease in redox peak potential, most likely caused by the lower reduction potential of the newly substituted tungsten addenda atoms. These results suggest that mixing PMo12 and PW12 in different molar ratios results in varying amounts of addenda atom substitution and a product that is very similar to that prepared by the conventional standard method for mixed addenda synthesis. Thus, with this approach, tuning POM redox behavior through addenda atom substitution becomes a simple and efficient process. This ability to easily make predictable and significant adjustments to POM redox properties is invaluable when designing electrodes to achieve desired pseudocapacitive characteristics.

**Multi-layer Polyoxometalate Electrodes**

*Surface engineering with Mo based polyoxometalates.—* POM mixtures can be used in conjunction with multi-layer modification...
Figure 4. Schematic of POM mixed addenda synthesis by simple mixing (A). Cyclic Voltammogram (CV) of a MWCNT electrode modified with a 3:1 molar mixture of PMo$_{12}$-PW$_{12}$ compared with that of a MWCNT electrode modified with PMo$_9$W$_3$ prepared by literature described methods (B).

Figure 5. Cyclic Voltammograms (CVs) of bare, pure GeMo$_{12}$, pure SiMo$_{12}$, and equimolar mixed GeMo$_{12}$-SiMo$_{12}$-modified MWCNT electrodes at 100 mV s$^{-1}$ (A). Cyclic Voltammograms of bare, pure PMo$_{12}$, and equimolar mixed GeMo$_{12}$-SiMo$_{12}$-modified MWCNT electrodes at 100 mV s$^{-1}$. A simple model representing the direct addition of the GeMo$_{12}$-SiMo$_{12}$ and PMo$_{12}$ curves is also plotted (gray line) as a prediction of the dual layer CV (B).

to combine the effects of multiple POMs for increased charge storage and a more ideally shaped CV profile. To be effective, this surface engineering approach requires POM chemistries that show different yet complementary redox features. For instance, we have previously reported the synthesis of GeMo$_{12}$O$_{40}^{4-}$ (GeMo$_{12}$), a custom POM chemistry that shows charge storage complementary to that of the commercially available SiMo$_{12}$O$_{40}^{4-}$ (SiMo$_{12}$) molecule. To take advantage of this complementary behavior, GeMo$_{12}$ can be combined with SiMo$_{12}$ in an equimolar mixed coating layer. The resulting CV for the GeMo$_{12}$-SiMo$_{12}$ mixed layer-modified CNT is shown in Figure 5A along with the pure component CVs for comparison. Since GeMo$_{12}$ and SiMo$_{12}$ both contain molybdenum heteroatoms, there is no possibility for mixed addenda synthesis so the mixed layer CV appears as a weighted combination of GeMo$_{12}$ and SiMo$_{12}$ profiles. Combining the overlapping GeMo$_{12}$ and SiMo$_{12}$ redox peaks makes for a broader mixed layer profile. However, the GeMo$_{12}$-SiMo$_{12}$ CV still does not have an ideal rectangular shape and there are clear gaps in the charge storage centered around +0.15 and –0.10 V.

To improve upon this performance, an additional POM layer can be superimposed in order to add more overlapping redox features to the profile. The task becomes more difficult as this additional POM chemistry must show redox features complementary to those of both GeMo$_{12}$ and SiMo$_{12}$. Figure 5B shows the CV of the GeMo$_{12}$-SiMo$_{12}$ electrode overlaid with that of PMo$_{12}$, another molybdenum based molecule. Our previous results have shown that the CVs of multi-layer POM electrodes demonstrate an additive combination of constituent layers. To predict the CV shape of a dual-layer electrode with a PMo$_{12}$ layer superimposed on a GeMo$_{12}$-SiMo$_{12}$ layer, a simple model showing the direct addition of the GeMo$_{12}$-SiMo$_{12}$ and PMo$_{12}$ CV curves is plotted along with the experimental data in Figure 5B (gray line). The charge storage of these constituent layers is not complementary; rather the redox peaks of PMo$_{12}$ almost directly overlay those of the GeMo$_{12}$-SiMo$_{12}$ electrode. The result is a model of the dual layer CV that shows enhanced capacitance, but retains a shape that is no more rectangular than that of the single layer, still showing prominent gaps in charge storage at +0.15 and –0.1 V. The redox behavior of PMo$_{12}$ is too similar to that of the other molybdenum based POMs. There is clearly a limit to the amount the POM redox properties can be tuned without changing the addenda atom. However, this limitation may be overcome by introducing the tungsten addenda atom via simple solution-based mixed addenda synthesis.

Surface engineering with mixed addenda polyoxometalates.— Substituting molybdenum addenda atoms for tungsten in PMo$_{12}$...
allows for more significant adjustments to the electrochemistry of the molecule. With the mixing approach these adjustments can be made in a simple yet precise manner, enabling the design of more effective molecular coatings. For instance, by mixing PW12 into the PMo12 coating solution and promoting addenda atom substitution, the redox peaks of PMo12 can be easily adjusted to smooth the peaks and fill in the charge storage vacancies demonstrated in the model shown in Figure 5B. Figure 6 shows the CV of the GeMo12-SiMo12 electrode overlaid with that of the 3:1 PMo12-PW12 electrode. As demonstrated, this PMo12-PW12 mixture results in addenda atom substitution, which shifts the second and third redox features of PMo12 to lower potentials, creating a series of almost perfectly overlapping redox peaks when overlaid with the GeMo12-SiMo12 CV. As a result, the predicted dual layer CV model (gray line in Figure 6) shows no sharp peaks or gaps, but rather a broad profile with charge storage that is very well distributed throughout the voltage window. When the actual dual layer GeMo12-SiMo12 (1:1)//PMo12-PW12 (3:1) electrode was fabricated through LbL deposition, the resulting CV (black line in Figure 6) was quite similar to that of the model in terms of both current density and shape. The dual layer profile demonstrates relatively constant charge and discharge currents allowing for a near rectangular CV that mimics the ideal shape of benchmark pseudocapacitive materials such as RuO2.

The capacitance values of the bare, single layer-modified, and dual layer-modified electrodes as a function of scan rate are summarized in Figure 6B. At 50 mV s⁻¹, the bare MWCNT electrodes have a volumetric capacitance of 16.4 F cm⁻³. With just a single POM active layer capacitance can be increased five to six fold, as demonstrated by the capacitance of 84.8 and 101.2 F cm⁻³ of the mixed PMo12-PW12 (3:1) and mixed PMo12-GeMo12 (1:1) electrodes, respectively. After dual layer modification, not only does the electrode show a more ideally shaped CV profile, but it also demonstrates further enhanced charge storage with a capacitance of 181.2 F cm⁻³, over eleven times larger than the EDLC capacitance of the bare CNT. As the majority of this capacitance is achieved over a relatively modest potential window of 0.7 V, the POM composites may be best suited to asymmetric device configurations. There is also the potential for exploring new POM chemistries with more positive redox potentials in an effort to extend the charge storage window. The methodology presented above is a promising approach for leveraging POMs to engineer the surface of carbon materials for desired performance.

In addition to large capacitance, the POM-modified electrodes also demonstrate excellent high rate performance. Even at 1 V/s the dual layer electrode maintains a capacitance of 141.2 F cm⁻³, close to 78% of its low-rate value. This type of high rate capability, rare for pseudocapacitive electrodes, results from the fast electron transfer kinetics of the POM cluster. The good overall conductivity of the electrodes may also be due to the intimate contact between the carbon substrate and the POM active layer. Figure 7 shows the SEM images of bare, single layer PMo9W3-modified, and dual layer GeMo12-SiMo12

Figure 6. Cyclic Voltammograms (CVs) of bare, equimolar mixed GeMo-SiMo-modified, PMo9W3-modified, and dual layer GeMo12-SiMo12 (1:1)//PMo12-PW12 (3:1) -modified MWCNT electrodes at 100 mV s⁻¹. A simple model representing the direct addition of the GeMo12-SiMo12 and PMo9W3 curves is also plotted (gray line) as a prediction of the dual layer CV (A). Capacitance vs. scan rate for POM-modified MWCNT electrodes (B).

Figure 7. SEM micrographs of A) bare MWCNT, B) single layer mixed 3:1 PMo12-PW12-coated MWCNT, and C) dual layer GeMo12-SiMo12 (1:1)//PMo12-PW12 (3:1)-coated MWCNT.
When PMo12 and PW12 solutions are used to modify MWCNT, the resulting mixed layer electrodes demonstrated their own characteristic redox activity, similar to that of PMo12 but with broader redox peaks that were shifted to lower potentials. This behavior can be attributed to a chemical change that takes place when PMo12 and PW12 are combined in solution which results in the formation of the mixed addenda PMo12-PW12 molecules. For instance, a mixed solution of PMo12 and PW12 in a 3:1 molar ratio results in the synthesis of PMo6W3 which has a 3:1 ratio of Mo to W addenda atoms. This simple mixing approach may not result in complete conversion to PMo6W3; however the mixed addenda product is very similar that achieved by the current literature standard method for mixed addenda synthesis. The detailed mechanism behind this addenda atom substitution and its applicability to alternative POM chemistries will be explored in future work.

The electrochemical behavior of the PMo12-PW12 mixtures demonstrated that the addenda atom substitution causes the shifting of redox peaks. As more W is incorporated into the molecule, its second and third redox peaks shift proportionally to lower potentials. This behavior can be attributed to alternative POM chemistries will be explored in future work.

The multi-layer approach can then be employed to modify a carbon substrate with the developed nanometer scale molecular coatings which incorporate the optimal POM combination. This methodology was used to fabricate dual layer electrodes which superimposed a mixed 3:1 PMo12-PW12 layer on a mixed 1:1 GeMo12-SiMo12 layer. The dual layer electrode had a capacitance over one hundred times larger than the EDLC, while demonstrating a close to rectangular CV shape due to the overlapping redox features of the POM combination. The POM composite also showed excellent performance at scan rates up to 1 V/s, owing to the highly reversible redox reactions of the POM molecule and their intimate contact with the carbon substrate. These results demonstrate that POM surface engineering, streamlined by the novel mixed addenda synthesis, is a promising strategy for designing molecular coatings to achieve desired pseudocapacitive characteristics.

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