

Final Report

Novel Electrochemical Process for Treatment of Perchlorate in Waste Water

SERDP Project ER-1433

MARCH 2011

Yuehe Lin
Pacific Northwest National Laboratory

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1. REPORT DATE (DD-MM-YYYY) 03/06/2011		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) May 2007 - March 2011	
4. TITLE AND SUBTITLE Novel Electrochemical Process for Treatment of Perchlorate in Waste Water				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Yuehe Lin, Ph.D.				5d. PROJECT NUMBER ER-1433	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Pacific Northwest National Laboratory (PNNL)				8. PERFORMING ORGANIZATION REPORT NUMBER ER-1433	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program 901 North Stuart Street, Suite 303 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) SERDP	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER-1433	
12. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <p>The presence of toxic perchlorate in the environment is a growing public health and environmental health concern. Military munitions and the chemical and nuclear industries are major sources contributing to the presence of perchlorate in the natural environment. Perchlorate is very stable in the environment and difficult to remove with conventional techniques. Novel technologies are needed for removing perchlorate in the environment in a simple, fast, cost-effective, and environmentally friendly manner. At the Pacific Northwest National laboratory, we developed an electrically switched ion exchange (ESIX) system based on a conducting polymer/carbon nanotube nanocomposite for removing perchlorate from drinking water and wastewater. The ESIX technology combines ion exchange and electrochemistry to provide a selective and reversible method for removing target species from wastewater. In this technique, an electroactive ion exchange layer is deposited on a conducting substrate, and ion uptake and elution are controlled directly by modulating the potential of the layer, resulting in a highly efficient use of electrical energy. The elu</p>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 39	19a. NAME OF RESPONSIBLE PERSON Yuehe Lin
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code) 509-376-0529

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Acronyms

BV	bed volume
CF	carbon fleece
CNT	carbon nanotube
CV	cyclic voltammetry
CVD	chemical vapor deposition
DoD	U.S. Department of Defense
EDL	electrical double layer
EPA	U.S. Environmental Protection Agency
EQCM	electrochemical quartz crystal microbalance
ESIX	electrically switched ion exchange
FE-SEM	field emission-scanning electron microscope
MWCNT	multi-wall carbon nanotube
PNNL	Pacific Northwest National Laboratory
PPy	polypyrrole
Py	pyrrole
SEM	scanning electron microscopy
SON	statement of need
XPS	X-ray photoelectron spectroscopy

Acknowledgments

This work is supported by the SERDP program. The research described in this paper was partially performed at Environmental Molecular Science Laboratory (EMSL), a national scientific user facility sponsored by the US DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated for DOE by Battelle under Battelle under Contract DE-AC05-76RL01830. The scientists and engineers working in this project for material synthesis and ESIX process development include Dr. Jun Wang, Dr. Xiaoli Cui, Dr. Daiwon Choi, Dr. Yuyan Shao, Dr. Jagan Bontha, Dr. Michael Ligla, and Dr. Xinhuan Kang. The material characterization was performed by Dr. Chongmin Wang for the transmission electron microscopy, Mr. Bruce Arey for the scanning electron microscopy, and Mr. Mark HEngelhard for the X-ray photoelectron spectroscopy. Mr. Wayne C Cosby helped on editing the final report.

Executive Summary

The presence of toxic perchlorate in the environment is a growing public health and environmental health concern. Military munitions and the chemical and nuclear industries are major sources contributing to the presence of perchlorate in the natural environment. Perchlorate is very stable in the environment and difficult to remove with conventional techniques. Novel technologies are needed for removing perchlorate in the environment in a simple, fast, cost-effective, and environmentally friendly manner. At the Pacific Northwest National laboratory, we developed an electrically switched ion exchange (ESIX) system based on a conducting polymer/carbon nanotube nanocomposite for removing perchlorate from drinking water and wastewater. The ESIX technology combines ion exchange and electrochemistry to provide a selective and reversible method for removing target species from wastewater. In this technique, an electroactive ion exchange layer is deposited on a conducting substrate, and ion uptake and elution are controlled directly by modulating the potential of the layer, resulting in a highly efficient use of electrical energy. The elution solution can be used repeatedly, minimizing secondary wastes and reducing costs normally required for standard ion exchange waste treatment. This project has used conductive nanocarbon materials as the support for electrochemically fabricating a conducting polymer nanostructure and for improving the stability and electrochemical properties of an electroactive ion exchanger. The electroactive ion exchanger nanocomposite has been incorporated into a flow reactor to selectively remove the perchlorates in wastewater. The results indicate that the ESIX technology is effective and selective for perchlorate removal and can potentially be used for large-scale treatment of wastewater.

1. Objectives

Perchlorate anion is used as a critical component in munitions used for combat and training. Perchlorate salts are also used in various chemical products, such as leather, rubber, fabrics, paints, and aluminum. As a result, perchlorate contamination is now recognized as a widespread concern affecting many water utilities. Highly soluble and mobile in water, perchlorate is generally very stable in the dissolved state. The potential for perchlorate occurrence in drinking water and food supplies is a human health concern because it can interfere with iodide uptake by the thyroid gland and thus result in decreased thyroid hormone production. It may also cause mental retardation in fetuses and infants. In 1998, the U.S. Environmental Protection Agency (EPA) formally added perchlorate to the contaminant candidate list for drinking waters. The EPA is now assessing health and ecological risks of perchlorate as well as considering a new standard for perchlorate in drinking water. The statement of need (SON) “CPSON-05-05: Treatment of Perchlorate in Water” calls for developing a new technology that demonstrates potential technological and cost advantages over existing technologies. The new technology should be capable of removing perchlorate ion to as low as a 1-ppb level to meet the drinking water standard that may be set in the future. The SON also calls for work that will result in information that ultimately guides the U.S. Department of Defense (DoD) in deciding whether there is a need for perchlorate treatment as well as what treatment technology should be selected on and off military installations.

In response to the SON “CPSON-05-05”, PNNL proposed developing a conducting polymer-based electrically switched ion exchange (ESIX) system for effectively treating the perchlorates in wastewater. The technology uses a PNNL developed conductive polymer nano-composite material as the electroactive ion exchange layer for selectively removing perchlorate from contaminated waters. The objective of this research was to demonstrate the effectiveness of the ESIX system based on a conducting polymer/carbon nanotube (CNT) nanocomposite for removing perchlorate from drinking water and wastewater. The following efforts are necessary to achieve this goal; 1) employ CNTs to improve the stability and the ion exchange properties of nanostructured conducting polymer on a substrate for effectively treating perchlorates in water, 2) study the influence of other anions on the removal of perchlorate, 3) optimize operations for the polypyrrole (PPy)/CNT nanocomposite, 4) study the ESIX flow reactor for treating perchlorate in water, and 5) treat wastewater using the above-developed devices and techniques and demonstrate the technology as a new and cost-effective approach for removing perchlorate from wastewaters.

2. Background

It is well known that perchlorate is a health concern because it can block the uptake of iodine in the thyroid gland when ingested, affecting the production of thyroid hormones. Recently, EPA set the safe dose for perchlorate at 0.7 μg per kg of body weight per day, a level recommended by the National Research Council (Hogue 2005). Perchlorate anion is used as a critical component in munitions for combat and training. Perchlorate salts are also extensively used in various chemical productions, such as leather, rubber, fabrics, paints, and aluminum. As a result, perchlorate contamination is now recognized as a widespread concern affecting many water utilities. Thus, removing perchlorate and treating perchlorate-contaminated groundwater (Kim and Gurol 2005, Gu et al. 2003, Cang et al. 2004) and milk as well as determining perchlorate ions (Lizondo-Sabater et al. 2004, Krynitsky et al. 2004) are of special importance. Because of its solubility and non-reactivity, perchlorate is a very stable substance in an aquatic system and is therefore difficult to remove. Several approaches, such as an ion exchange method based on culture (Cang et al. 2004), selective anion exchange (Gu et al. 2002, 2005), microbial and biological reduction (Sturchio et al. 2003, Coates and Achenbach 2004), and electrochemical and chemical reduction (??), have been evaluated. These technologies still have some technical limitations, they generate substantial secondary wastes, and they are costly. It is an urgent necessity to develop innovative, cost-effective, and green technology for treating perchlorate from wastewaters.

3. Materials and Methods

The objective of this project is to develop an ESIX system based on a conducting polymer/CNT nanocomposite for removing perchlorate from wastewater.

The initial work focused on synthesizing and characterizing the conducting polymer/CNT nanocomposite. Then the nanocomposite film was effectively fabricated on an electrochemical flow reactor, and the ESIX flow reactor has been used to study 1) perchlorate ion uptake, 2) the elution of anions, 3) the selectivity of ESIX for perchlorate, and 4) the lifetime of the PPy/CNT nanocomposites. Figure 1 illustrates the principle of the ESIX unit for uptake and elution of perchlorates. When the oxidation potential is applied to the electrode, PPy is oxidized, and the polymer surface is positively charged; therefore, perchlorate is absorbed in the film to keep the film neutral [Figure 1(a)]. However, when the electrode is applied with the reduction potential, the PPy will be reduced, and there are no charges in the PPy film. Therefore, the perchlorate will be forced out [Figure 1(b)].

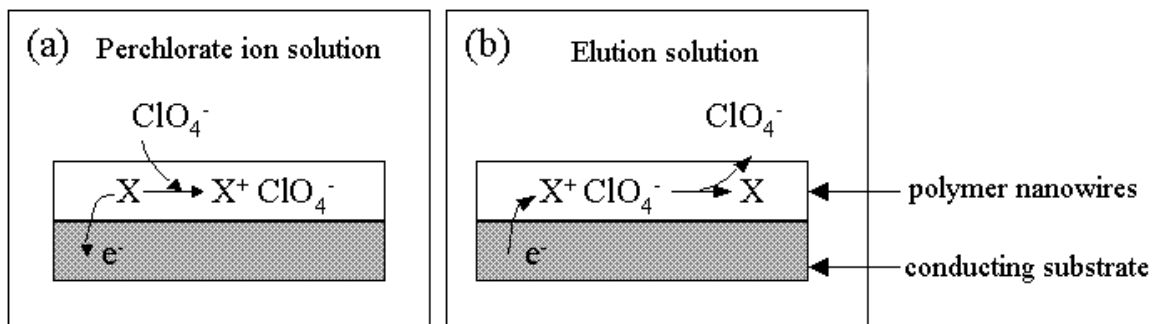


Figure 1. Illustration of the Principle of the ESIX Unit for Uptake and Elution of Perchlorates

The nanostructured conducting polymer/CNT composites on a conducting substrate have a large specific surface area. There are several advantages to using this nanocomposite EXIS: 1) a large loading capacity for anions, 2) a fast exchange rate, and 3) a long lifetime. This approach takes advantage of the unique properties of a conducting polymer—when the polymer is in an oxidized state, anions will be adsorbed in the film. While it is in a reduced state, anions will be driven out of the film because of keeping the film neutral; electrochemical technology can modulate the loading of the anions in the film or the eluting of the anions out of the film by switching the electrochemical potential or the current on the conducting substrates. Therefore, the system can remove perchlorates in wastewater.

The project includes several tasks: 1) employing CNTs to improve the stability and the electrochemical properties of a conducting polymer on a substrate for effectively treating perchlorates in water, 2) studying the influence of other anions on the removal of perchlorate, 3) optimizing operational conditions for the PPy/CNT nanocomposite, 4) developing a laboratory-scale ESIX flow reactor and demonstrating effective removal of perchlorate from water.

4. Results and Discussion

4.1 Synthesize Polypyrrole/Carbon Nanotube Nanocomposites

4.1.1 Growth of CNT Array on Carbon Fiber Paper and Deposition of Conductive Polypyrrole Polymer on CNT Arrays

CNT arrays on porous carbon fiber paper were fabricated by coating the carbon fiber paper with chromium. The chemical vapor deposition (CVD) technique was used to grow CNTs that were 80 nm in diameter and 2 μm in length. The density was 10^9 CNT/ cm^2 . Figure 2(a-c) shows the scanning electron microscopy (SEM) images of carbon fiber paper and a CNT array grown on carbon fiber paper.

Pyrrole (Py) deposition was carried out by both the chronoamperometry and cyclic voltammetry (CV) modes of electrochemical deposition using a 0.2 M NaCl and 0.1 M Py solution. An electrochemical deposition and a test were performed with a CHI 400A electrochemical workstation (CH Instruments, Inc., Austin, TX) in a conventional three-electrode setup with a platinum wire counter electrode and an Ag/AgCl reference electrode. However, the chronoamperometry mode showed better control due to continuous deposition, which can be completely controlled by the deposition time. The morphology of the electrochemically deposited CNT/PPy composite was characterized with a Zeiss Leo 982 field emission-scanning electron microscope (FE-SEM) equipped with a backscatter detector. Figure 2(e-h) shows the PPy coating of the CNT array electrode with a different deposition time, which resulted in a different thickness of the PPy thin film. The PPy-coated, CNT array electrodes were uniform without losing the original morphology.

Figure 3 shows current vs. time during the electrochemical deposition of PPy on a different electrode substrate. The highest current was observed for the CNT array grown on the carbon fiber paper electrode. No significant current was observed when no Py was added to the 0.2 M NaCl solution.

Compared to PPy deposited on only a carbon paper electrode without a CNT array, a randomly oriented CNTs (multi-wall carbon nanotube [MWCNT], >95% purity, OD: 20~30 nm, L: 10~30 μm , Cheap Tubes, Inc.) on a double-stick carbon tab showed a higher deposition current, indicating a better PPy coating on the CNTs and a higher surface area of the electrode. The PPy deposition on a CNT array grown on carbon fiber paper was an order of magnitude higher than randomly oriented CNTs on the carbon tab.

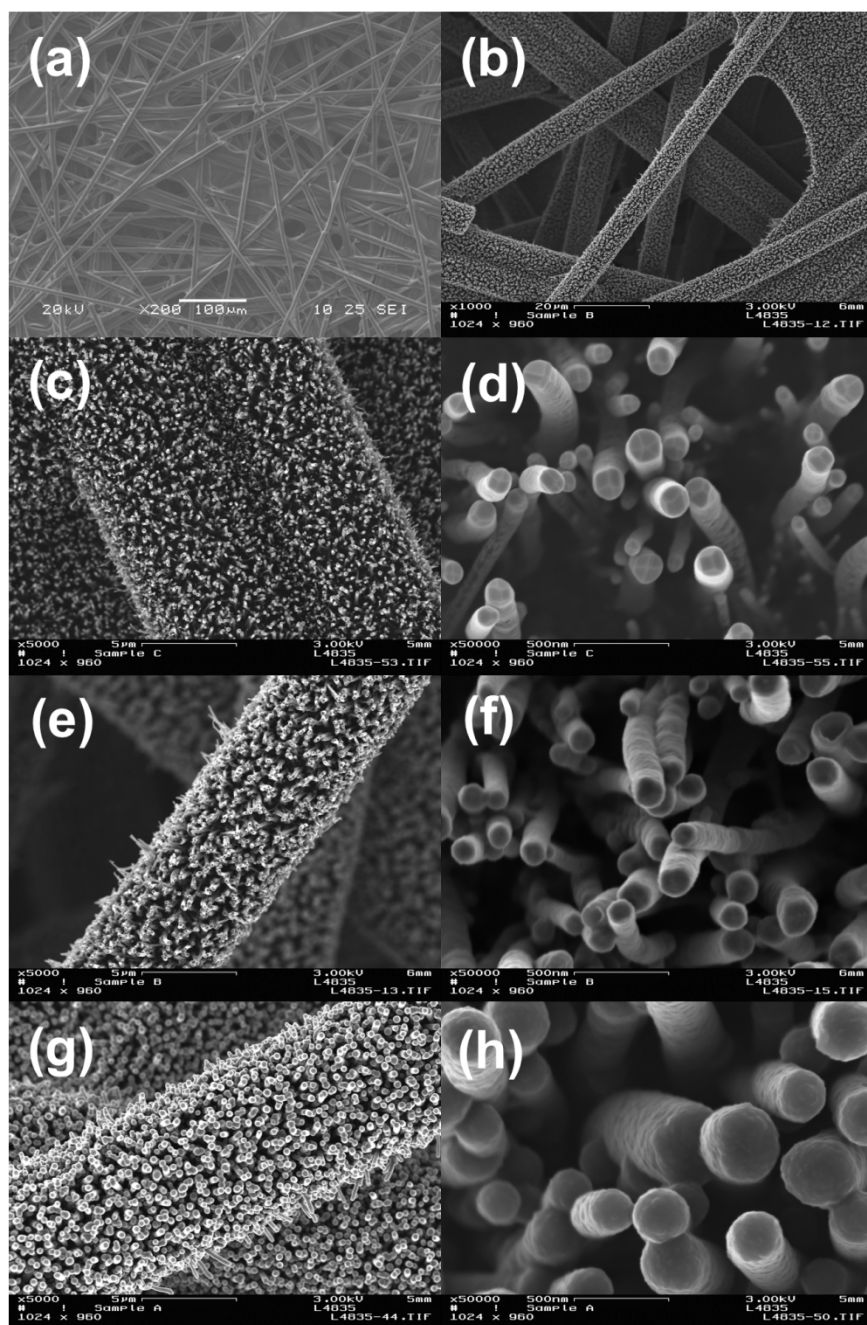


Figure 2. SEM Images of (a) Carbon Fiber Paper, (b-d) CNT Array Grown on Carbon Fiber Paper, (e, f) PPy Deposited on CNT Array/Carbon Fiber Paper at 0.7 V for 150 s, and (g, h) PPy Deposited on CNT Array/Carbon Fiber Paper at 0.7 V for 600 s

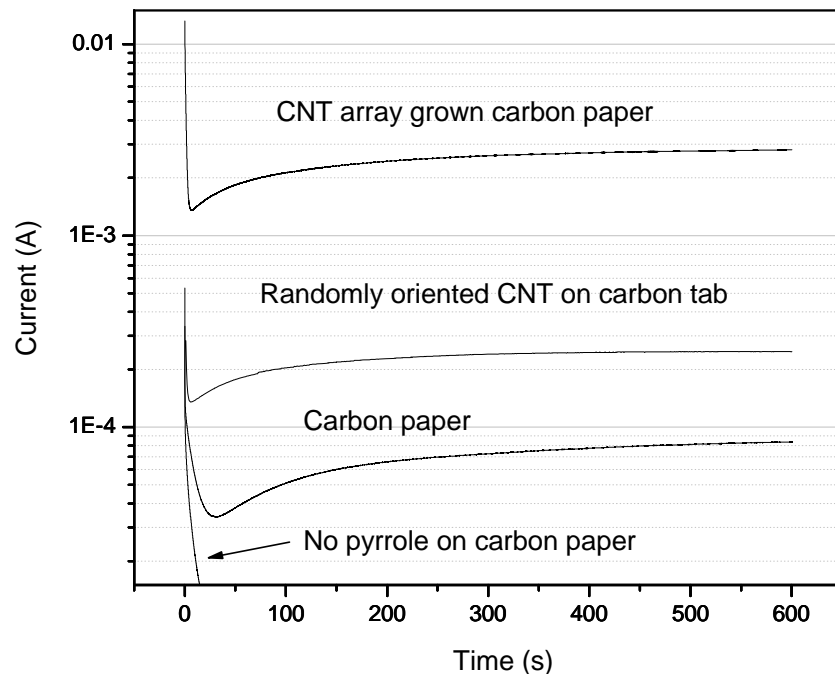


Figure 3. Electrochemical Deposition of PPy by Chronoamperometry on Various Substrates at 0.7 V for 600 s

Figure 4 shows the CV of PPy deposited on carbon paper with and without growing a CNT array. A significantly higher current density observed shows that the electroactive surface area of PPy on the CNT array is much higher than that without CNT array support. This shows the important role of nanostructuring of the electrode. Figure 5 shows the desorption and adsorption of chlorine and perchlorate anions while cathodic and anodic potentials were applied. In this case, a significantly higher current was observed for the PPy-coated CNT array grown on a carbon fiber paper electrode, indicating the enhanced ion-exchange property of the CNT array electrode.

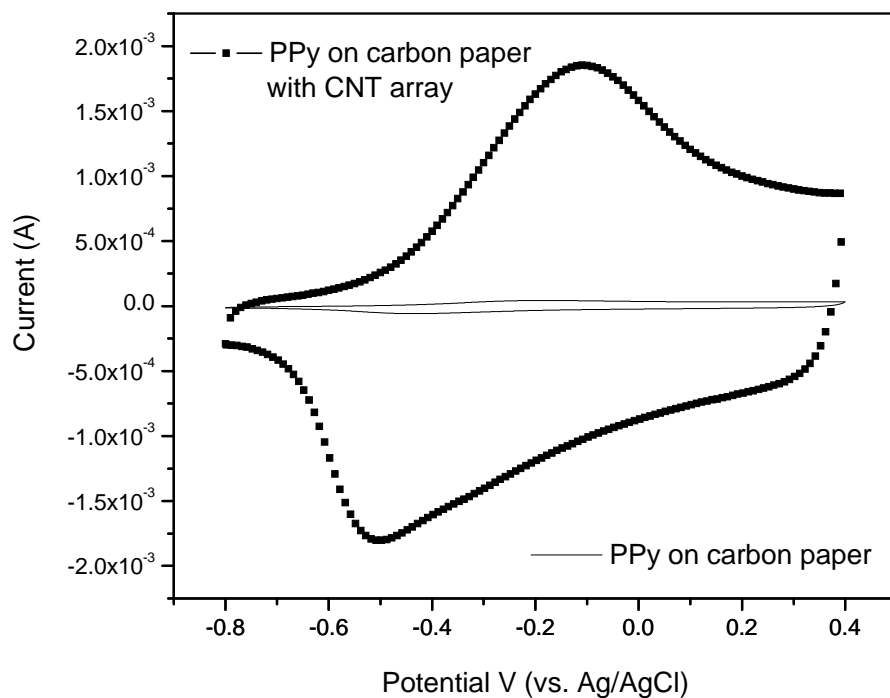


Figure 4. CV of PPY Deposited on Carbon Paper with and Without CNT Array in 0.2 M NaCl Solution Scanned at 5 mV/s

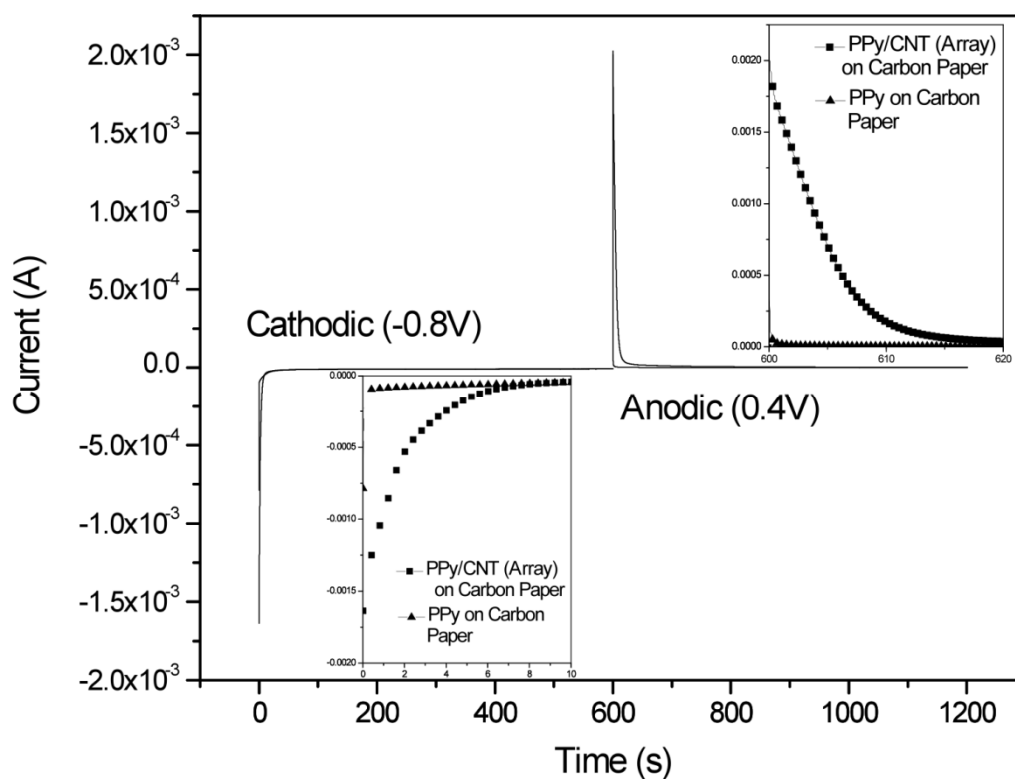


Figure 5. Chronoamperometry of PPY Deposited on Carbon Paper with and Without CNT Array in 0.2 M NaCl/0.02 M NaClO₄ Solution

Figure 6 shows the morphologies of the randomly oriented CNTs on a carbon tab and CNT/PPy nanocomposites synthesized on both the carbon tab and the gold-coated quartz crystal. The CNT/PPy composite electrode was fabricated on a gold-coated, quartz crystal electrode for electrochemical quartz crystal microbalance (EQCM) analysis for understanding the weight change during electrochemical PPy deposition and testing in various anion solutions. The SEM images of randomly dispersed CNTs and CNT/PPy that were synthesized on a carbon tab are shown in Figure 6(a) and (b). This shows the slightly more packed structure of the CNT/PPy. However, the CNT/PPy composites retain their CNT backbone structure via a uniform PPy coating of CNTs, creating a high-surface-area electrode. The smooth gold surface exposed in Figure 6(c) indicates that most of the Py unit is adsorbed on the CNT surface before electropolymerization, thereby coating PPy mostly on the CNT surface.

The CNT/PPy film on gold-coated quartz crystal was prepared via *in situ* electrochemical deposition. Due to the weight limitation of the quartz balance and dispersion of CNTs in aqueous media, a shorter MWCNT-COOH was used instead of the longer MWCNTs. The deposition solution was prepared by dispersing 3 mg of 0.5~2.0 μm long MWCNT-COOH in 5 mL of 0.2-M NaCl supporting electrolyte by sonication for 5 min followed by addition of Py (0.1 M). The solution was sonicated for 5 min before the deposition of CNT/PPy at a constant potential of 0.7 V vs. Ag/AgCl in an EQCM Teflon cell under a high-purity Ar flow. For comparison, pure PPy thin film was deposited using an identical solution without MWCNT-COOH present. The deposition was stopped when the CNT/PPy and PPy mass reached 2.52 μg ($\Delta f=1800$ Hz).

4.1.2 Electrochemical Deposition of PPy and CNT/PPy Composite

The deposition and change in the oxidation state during the electrochemical process of the conducting polymer is accompanied by mass changes. Hence, the EQCM was used to characterize the amount of loading of these polymers during deposition. The mass change (Δm) at the quartz crystal was calculated by measuring the frequency change (Δf) using the Sauerbery equation.

$$\Delta f = \frac{-2f_0^2}{A\sqrt{\mu\rho}}\Delta m \quad (1)$$

where f_0 = resonant frequency of the unloaded quartz crystal

Δm = mass change in grams

A = surface area of the electrode

ρ = density of the quartz crystal (2.648 g/cm³)

μ = sheer modulus of quartz (2.947 $\times 10^{11}$ dyne/cm²).

For the 8-MHz crystal, the mass change is 1.4 ng for a 1-Hz frequency change.

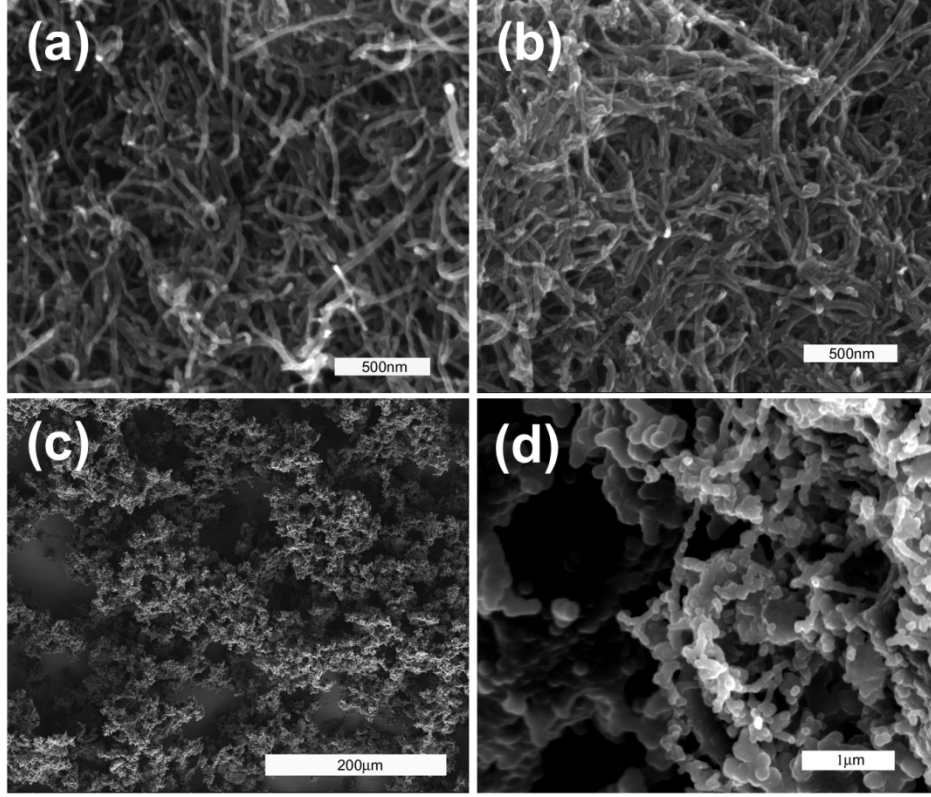


Figure 6. SEM Images of (a) MWCNTs on Carbon Tab, (b) PPy Deposited on MWCNTs for 150 s at 0.7V, (c) and (d) CNT/PPy Composite Deposited *in situ* on the Gold-Coated Quartz Crystal at 0.7 V for 600 s

Figure 7(a) shows the electrochemical deposition of the pure PPy and CNT/PPy composite on the gold-coated quartz electrode by applying a constant potential of 0.7 V. For PPy, a nearly linear weight gain and a charge increase with the time of deposition were observed. During the electro-polymerization of Py, a positively charged polymer chain is compensated via incorporating anions from the electrolyte solution. Therefore, the polymerization reaction can be described as follows:



where n is the degree of polymerization, and y is the anion doping level defined as the number of unit charges per Py ring. For one monomer unit formation, $(2 + y)$ electrons are required. Thus, the mass of PPy film originating from the above equation can be calculated using Faraday's law:

$$\Delta m = \frac{\Delta Q(M_{Py} + yM_{Cl})}{F(2 + y)} \quad S = \frac{\Delta m}{\Delta Q} = \frac{(M_{Py} + yM_{Cl})}{F(2 + y)} \quad (3)$$

where M_{Py} = molar mass of the monomer unit in the polymer (65 g/mol)
 M_{Cl} = molar mass of the Cl^- anion (35.5 g/mol)
 F = Faraday's constant (96,485.3 C/mol)
 S = slope of Δm versus ΔQ shown in Figure 7(a).

The calculated y value for PPy was 0.16 (one Cl^- ion per 6.25 Py unit), which is slightly lower than the previously reported y values (0.2~0.5) for PPy synthesized electrochemically. Compared to the PPy, the *in situ* deposition of CNT/PPy shows a much lower S slope ($\Delta m/\Delta Q$). The larger charge and lower mass increase with time indicates that Py monomers are not separated from the dispersed CNTs in the solution, but are possibly adsorbed on the CNT surface. Also, the high surface area of CNTs provides a much larger charge accumulation of the supporting electrolyte. Therefore, the current and the charge created during CNT/PPy deposition may not be solely from electro-polymerization of Py monomers. Figure 7(b) shows the electro-polymerization of PPy by CV from 0~0.8 V vs. Ag/AgCl where the initiation of PPy deposition started around 0.55 V vs. Ag/AgCl.

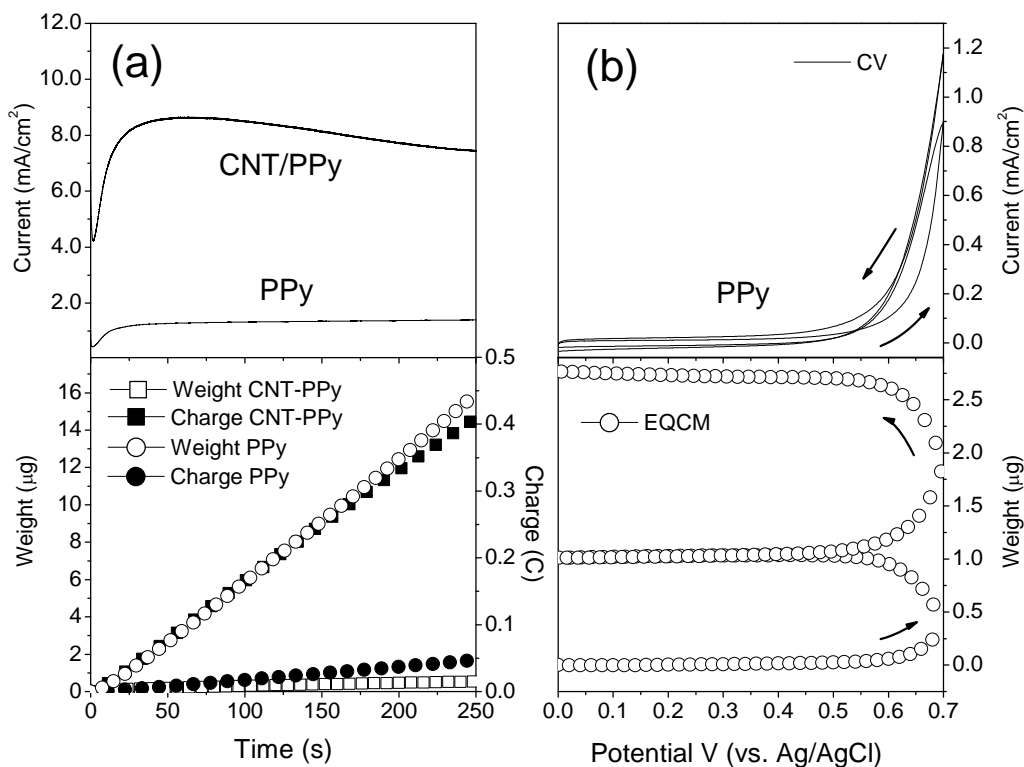


Figure 7. Electrochemical Deposition of (a) PPy and CNT/PPy by Chronoamperometry and (b) PPy by the CV Mode of EQCM

4.1.3 Cyclic Voltammetry-EQCM Measurements

Pure PPy and CNT/PPy composite electrodes in electrolytes containing different counter anions were investigated by the CV mode of EQCM as shown in Figure 8. All scans were performed at a scan rate of 5 mV/s between -0.8 V and 0.4 V vs. Ag/AgCl. Because both PPy and CNT/PPy were synthesized using a 0.2 M NaCl supporting electrolyte, the changes in CV were observed when exposed to different electrolytes. This is because the original counterion (Cl^-) was replaced by different anions in the electrolyte. Thus, all the electrodes were cycled four times in the respective electrolyte solution to reach an equilibrium condition before the EQCM measurements.

CV provides important information on the ion-exchange behavior between the conducting polymer and the outer electrolyte because the charging and discharging are associated with the redox process. The CV plots in Figure 8 show different CV shapes, depending on the electrolyte composition. Irrespective of the electrolytes used, a pure PPy thin film shows a much lower capacitance than the CNT/PPy composite because of the lower surface area available for electrical double layer (EDL) formation. The pure PPy thin films show a slightly sloped CV whereas CNT/PPy composite CVs are less sloped because of the higher ionic diffusion and electronic conductivity provided by CNTs. Sharp peaks observed near 0.2 V and -0.4 V of the CV plot correspond to the oxidation and reduction of PPy, respectively. During electrochemical cycling, the electroneutrality of a PPy can be preserved in different ways. On oxidation of the PPy polymer, absorption of anions or desorption of cations can occur. On the other hand, the PPy polymer can be reduced by the absorption of cations or the desorption of anions.

Figure 9 shows a schematic illustration of possible ion-exchange routes of PPy during the oxidation and reduction process. Consequently, both anions and cations play an important role in the redox process. However, it has been widely reported that, for low-molecular-weight inorganic anion-doped PPy, anions are mostly associated with insertion/extraction during the anodic/cathodic process while for polymeric anion-doped PPy, cation insertion/extraction also occurs.

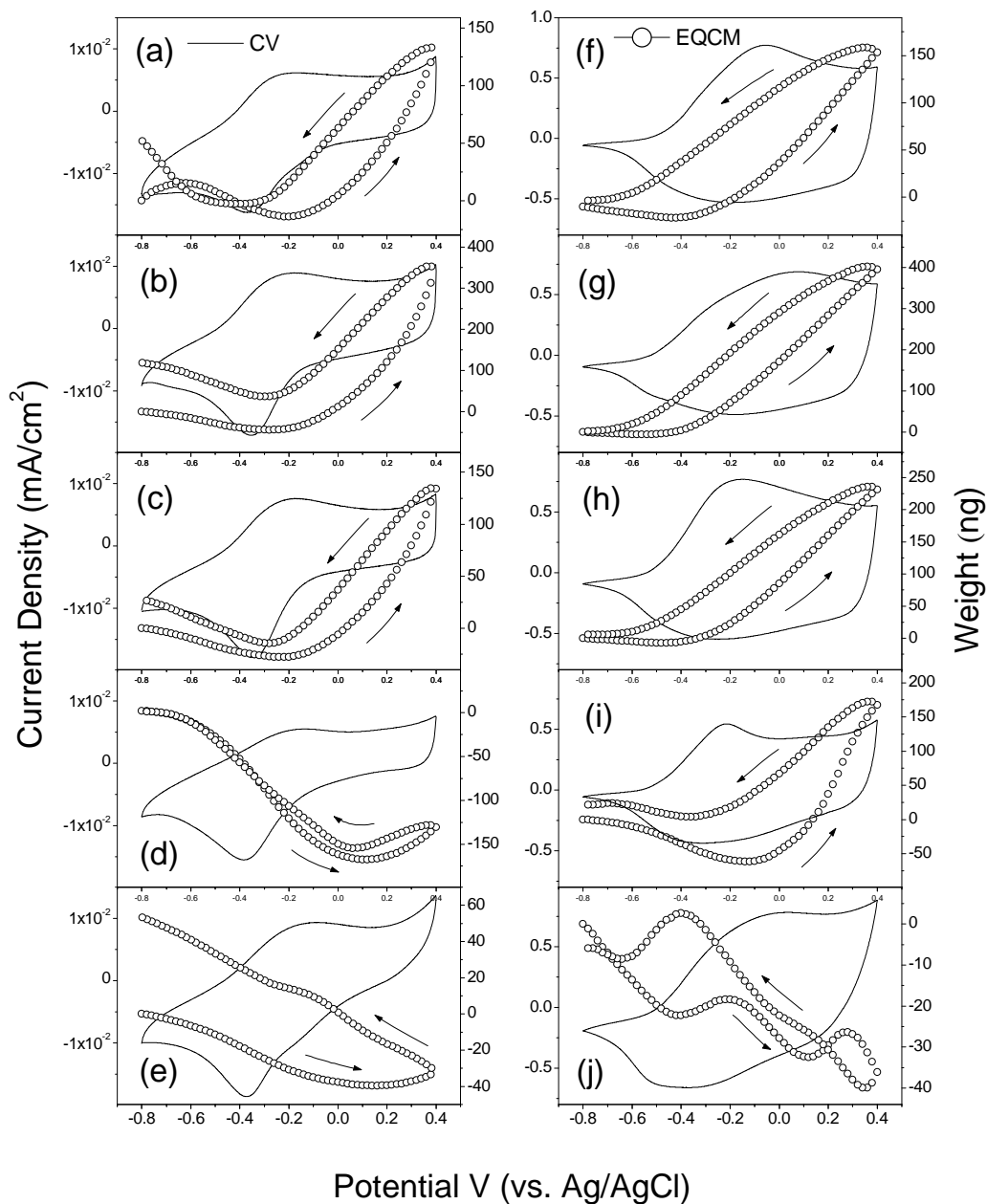


Figure 8. CV-EQCM of PPy in 0.2 M, (a) NaCl, (b) NaClO₄, (c) NaNO₃, (d) Na₂SO₄, (e) NaHCO₃ and CNT/PPy Composite in 0.2 M, (f) NaCl, (g) NaClO₄, (h) NaNO₃, (i) Na₂SO₄, and (j) NaHCO₃ Scanned at 5 mV/s Between -0.8 V and 0.4 V vs. Ag/AgCl

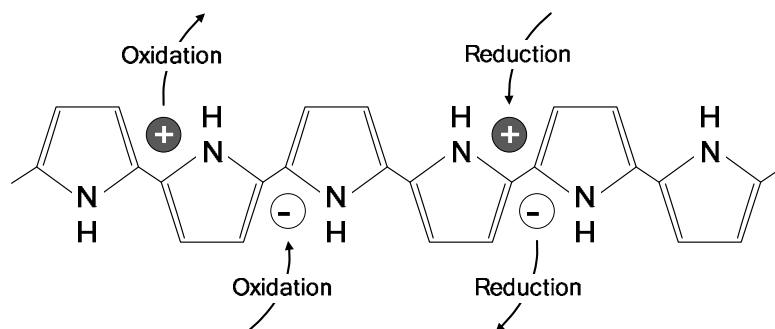


Figure 9. Schematic Illustration of Cation and Anion Exchange Mechanism of PPy Redox Reaction During Electrochemical Cycling

EQCM plots corresponding to CV results are shown in Figure 8 where the PPy thin film in 0.2 M NaCl, NaClO₄, and NaNO₃ electrolytes show an initial decrease in mass because of Na⁺ cation extraction followed by a mass increase at a higher potential by the insertion of anion species. However, PPy in Na₂SO₄ and NaHCO₃ solutions do not show a significant mass gain even at a higher potential region. Only a slight increase in mass was observed above 0.3 V in 0.2-M Na₂SO₄ electrolyte. The lower SO₄²⁻ absorption might be related to the faster Na⁺ diffusion or higher Na⁺ ion concentration in the solution. However, Na₂SO₄ was used to maintain close to neutral pH of the electrolyte for PPy stability. These results indicate that PPy cannot be effectively oxidized in a bivalent or larger anion solution. The extraction of Na⁺ ions shows the presence of Na⁺ ions in the PPy, which is likely incorporated during the synthesis and pre-cycling process, but the amount of Na⁺ in the PPy is unknown. Except for PPy in 0.2 M Na₂SO₄ electrolyte, cation and anion insertion/extraction during the complete cycle resulted in a net mass gain, suggesting either a diffusion limitation of ions in and out of the PPy film, or ionic species from solution are being bound after penetration into the PPy film. The consecutive cycling of PPy electrode resulted in a continuous mass increase followed by eventual saturation of PPy ion-exchange capacity. Such an ion-exchange limitation will lead to the instability of the PPy polymer and lower its redox activity.

Compared to PPy thin film, CNT/PPy nanocomposites show better anion insertion behavior. No initial mass loss corresponding to Na⁺ extraction has been observed, especially in NaCl, NaClO₄ and NaNO₃ electrolytes. Also, a significantly larger mass gain has been observed in the Na₂SO₄ solution. However, in the NaHCO₃ electrolyte, no distinguishable changes between PPy and CNT/PPy have been observed. The CNT/PPy composites in 0.2 M NaCl, NaClO₄, and NaNO₃ electrolytes show almost negligible net mass changes during a complete cycle, indicating that the ion-exchange is fully reversible. This is probably due to the fast ionic diffusion made possible by the high surface area and thinner coating of PPy on the CNT backbone. Such a reversible ion-exchange property of CNT/PPy relates to the stability of the electrode.

The anion loading capacity of pure PPy and CNT/PPy was calculated from the mass gain between the lowest and the highest point of EQCM during oxidation in respective electrolytes. When the mass change was divided by the molecular weight of each anion species, the molar capacity of anion in PPy was in the order of Cl⁻ > ClO₄⁻ > NO₃⁻ > SO₄²⁻ > CO₃²⁻, irrespective of the PPy or CNT/PPy electrode. The anion loading on PPy was 11 mole%, 10.6 mole%, and

6.9 mol% for Cl^- , ClO_4^- , and NO_3^- , respectively. This is equivalent to one Cl^- , ClO_4^- , and NO_3^- ion per every 9.1, 9.4, and 14.5 Py unit of PPy polymer, respectively. The anion loading capacity improved slightly by introducing CNT but, considering the amount of PPy in the CNT/PPy electrode, the loading capacity per PPy alone should be much higher than that of pure PPy because all measurements were conducted based on an equivalent weight of PPy and CNT/PPy deposited. This also suggests that the pure PPy thin film does not fully use its ion-exchange capacity, and only the outer layer may participate in the electrochemical process.

The stability of the CNT/PPy composite electrode was studied by consecutively cycling the PPy coated on randomly oriented CNT on a carbon tab electrode in 0.2 M NaCl solution up to 100 cycles as shown in Figure 10. A negligible decrease in current was observed even after 100 cycles, and the slight decrease in current is mostly due to incomplete anion/cation ion exchange because cycling was performed without complete elution of absorbed species. This shows that the PPy/CNT electrode can exchange ions reversibly without degrading the electrode.

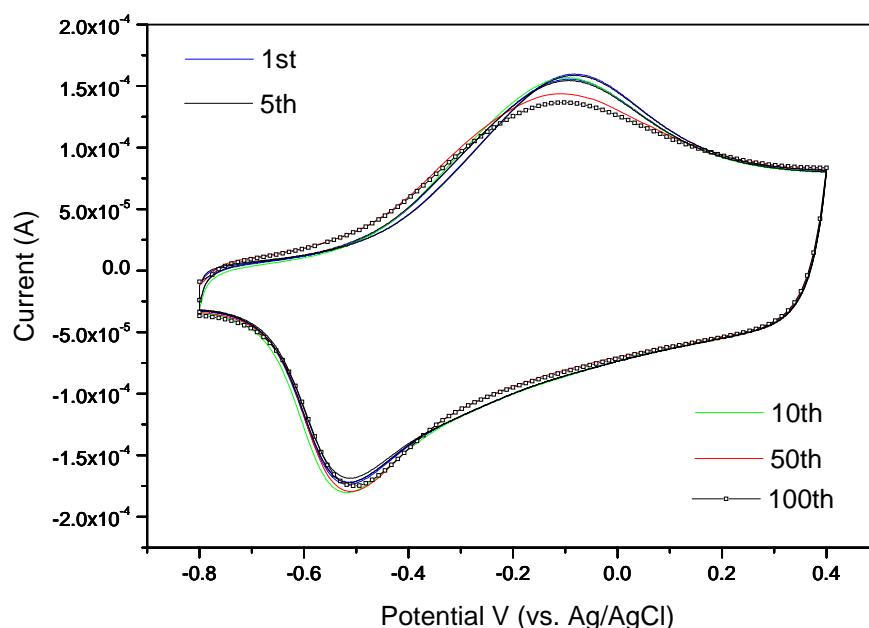


Figure 10. CV of PPy/CNT (randomly oriented) Electrode in 0.2 M NaCl Electrolyte from -0.8 V~0.4 V vs. Ag/AgCl at a Scan Rate of 5 mV/s up to 100 Cycles

4.2 Study Influence of Other Anions Using Batch Electrochemical Cell

The ion-exchange properties of PPy and CNT/PPy composites were evaluated by using both CV modes of EQCM. However, these results do not provide the relative affinities of respective anions to PPy polymer except that the carbonate ion does not participate in the ion-exchange process. Therefore, the affinity of these different anions to PPy polymer was further characterized by using X-ray photoelectron spectroscopy (XPS) on the PPy film after anion insertion. All electrodes were pre-cycled four times in respective electrolyte solutions to reach an equilibrium condition before actual anion insertion. Perchlorate ion (ClO_4^-) was chosen as the

standard anion since our previous results showed the PPy selectivity of perchlorate over the chlorine ion.

Figure 11 depicts survey scans of PPy/CNT (randomly oriented) film prepared in different electrolyte solutions after applying an anodic potential of 0.4 V for 300 s, and the results of elemental analyses are summarized in Table 1. The XPS measurements were performed on one sample under three different conditions to demonstrate the electrically switched anion-exchange and perchlorate selectivity of the PPy films. The first measurement was made with the as-prepared CNT/PPy film in a 0.2 M NaCl solution. To show the intake of ClO_4^- with the presence of Cl^- , the CNT/PPy electrode was held at a controlled potential of 0.4 V for 300 s in a solution containing 0.02 M NaClO_4 and 0.2 M NaCl. The elution of ClO_4^- and Cl^- out of the CNT/PPy film was confirmed by holding the CNT/PPy electrode at a cathode potential of -0.8 V for 300 seconds. As shown in Figure 11(a), two peaks of $\text{Cl}2p$ can be distinguished, suggesting that the ClO_4^- has been incorporated into the CNT/PPy film with the smaller Cl^- peak. After desorption, peaks corresponding to ClO_4^- and Cl^- disappeared, showing the reversibility of the CNT/PPy. The $\text{ClO}_4^-/\text{Cl}^-$ peak ratio of 0.5 implies 5 times better ClO_4^- selectivity over Cl^- , considering that there was a 10 times lower perchlorate concentration in the electrolyte. Figure 11(b), (c), and (d) shows XPS results of the CNT/PPy electrode oxidized at 0.4 V for 300 s in electrolyte containing 0.02 M NaClO_4 in 0.2 M Na_2SO_4 , NaNO_3 , and NaHCO_3 , respectively. The XPS peaks corresponding to ClO_4^- ions are observed with the presence of NO_3^- and SO_4^{2-} ion peaks. The ratios between $\text{ClO}_4^-/\text{NO}_3^-$ and $\text{ClO}_4^-/\text{SO}_4^{2-}$ were 0.16 and 0.2, respectively. However, only the strong ClO_4^- peak has been observed in NaHCO_3 electrolyte, and no traces of the CO_3^{2-} peak (290.2 eV) have been observed. In addition, a relatively larger amount of Na^+ ion (8.4 at.%) was observed for CNT/PPy in the NaHCO_3 electrolyte, which is likely to be introduced into the PPy during the pre-cycling step because sodium plays important role in electro-neutralizing the PPy. The cation can also enter the PPy film if the PPy film electrode is over oxidized at an anode potential for a long time. The affinity of anions to CNT/PPy was in the order of $\text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{CO}_3^{2-}$.

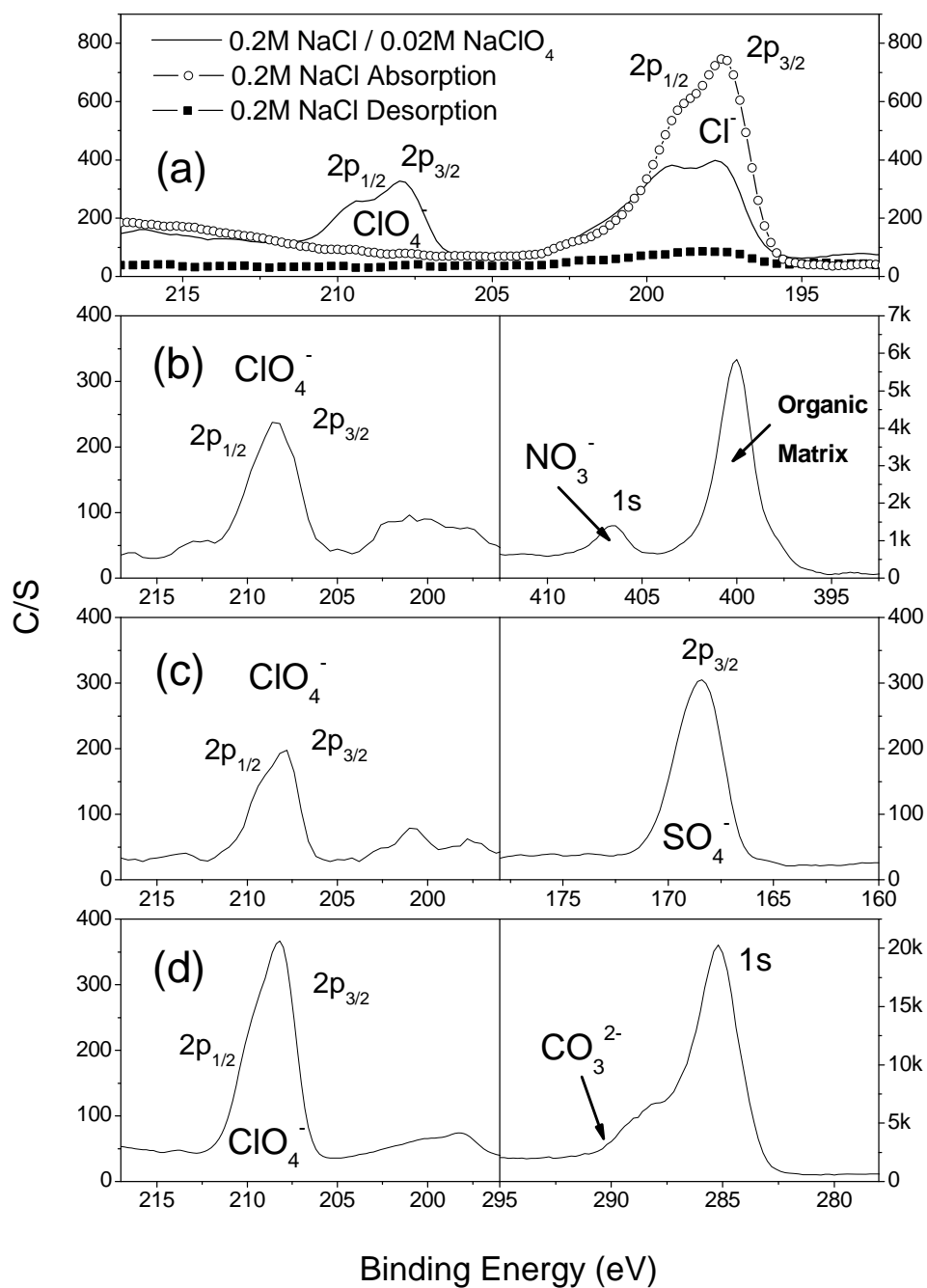


Figure 11. High-Resolution XPS Spectrum of CNT/PPy Thin Film Exposed to Electrolyte Containing 0.02 M NaClO₄ in (a) 0.2 M NaCl, (b) 0.2 M NaNO₃ (c), 0.2 M Na₂SO₄, and (d) 0.2 M NaHCO₃

Table 1. Surface Composition (in at.%) Calculated from High-Resolution XPS Spectrum of CNT/PPy Thin Film Exposed to Different Electrolytes Containing 0.02 M NaClO₄ in 0.2 M NaCl, 0.2 M Na₂SO₄, 0.2 M NaNO₃, and 0.2 M NaHCO₃

Peaks	C1s	N1s	N1s/NO ₃ ⁻	O1s	Na1s	S2p/SO ₄ ²⁻	Cl2p/Cl ⁻	Cl2p/ClO ₄ ⁻
NaCl Adsorption	67.0	10.3	-	19.5	1.2	-	0.75	0.01
NaCl/NaClO ₄ Adsorption	66.9	7.5	-	20.5	1.1	-	0.46	0.23
NaCl/NaClO ₄ Desorption	68.3	8.2	-	21.4	0.6	-	0.05	0.00
NaNO ₃ /NaClO ₄ Adsorption	58.6	8.5	1.2	26.0	1.5	-	0.07	0.19
Na ₂ SO ₄ /NaClO ₄ Adsorption	62.6	8.7	-	24.3	1.7	0.8	0.04	0.16
NaHCO ₃ /NaClO ₄ Adsorption	52.9	8.5	-	27.0	8.4	-	0.03	0.68

4.3 Optimize the Operational Conditions for Uptake and Elution of Perchlorate (Batch EC cell)

The chronoamperometry mode of EQCM was conducted to better understand the ion-exchange capacity and the kinetics of the PPy and CNT/PPy electrode in different anion solutions. The CV shows the detailed ion-exchange mechanism during the redox process whereas chronoamperometry provides information on equilibrium conditions at constant potential. Figure 12 shows the EQCM plot during the chronoamperometry mode of PPy and CNT/PPy in different electrolytes. The PPy shows a continuous mass gain up to 1000 s at 0.4 V whereas the CNT/PPy electrode reached full saturation within 100 seconds. These results show that the ion-exchange kinetics of PPy during oxidation has been improved more than 10 times by introducing the CNT backbone. The anion loading capacity of both PPy and CNT/PPy at constant potential is calculated and summarized in Table 2. The results indicate that both PPy and CNT/PPy electrodes have the highest loading capacity to ClO₄⁻. Since the Cl⁻ anions have a much smaller molecular weight than other anions, the molar capacity of the anion is in the order of Cl⁻ > ClO₄⁻ > NO₃⁻ > SO₄²⁻ > CO₃²⁻, which is the same as that observed previously in the CV-EQCM results. The reduction potential of PPy and CNT/PPy electrodes was chosen at 0 V and -0.8 V, respectively, because the elution of anions was observed at different potentials in CV-EQCM results. When pure PPy was reduced at -0.8 V, an increase in mass was observed because of Na⁺ ion incorporation, which coincides with the CV-EQCM results. Even at 0 V, the pure PPy did not fully extract all the absorbed anions because of poor reversibility of the PPy film. However, the CNT/PPy shows complete elution of absorbed anions at -0.8 V in 0.2 M NaCl, NaClO₄, and NaNO₃ electrolytes. The CNT/PPy in 0.2 M Na₂SO₄ electrolyte shows a weight increase at -0.8 V because Na⁺ ions are incorporated, which coincides with the CV-EQCM plot where the lowest weight was observed at -0.1 V. The CNT/PPy in 0.2 M NaHCO₃ electrolyte lost weight at 0.4 V, followed by a weight gain at -0.8 V, showing a reversed trend.

This is another indication of Na^+ ion participation during ion-exchange with extraction and insertion occurring at 0.4 V and -0.8 V, respectively. Hence, for the elution of absorbed anions, different potentials should be applied, and the uptake and release of ions can be controlled by modulating the potential of the film.

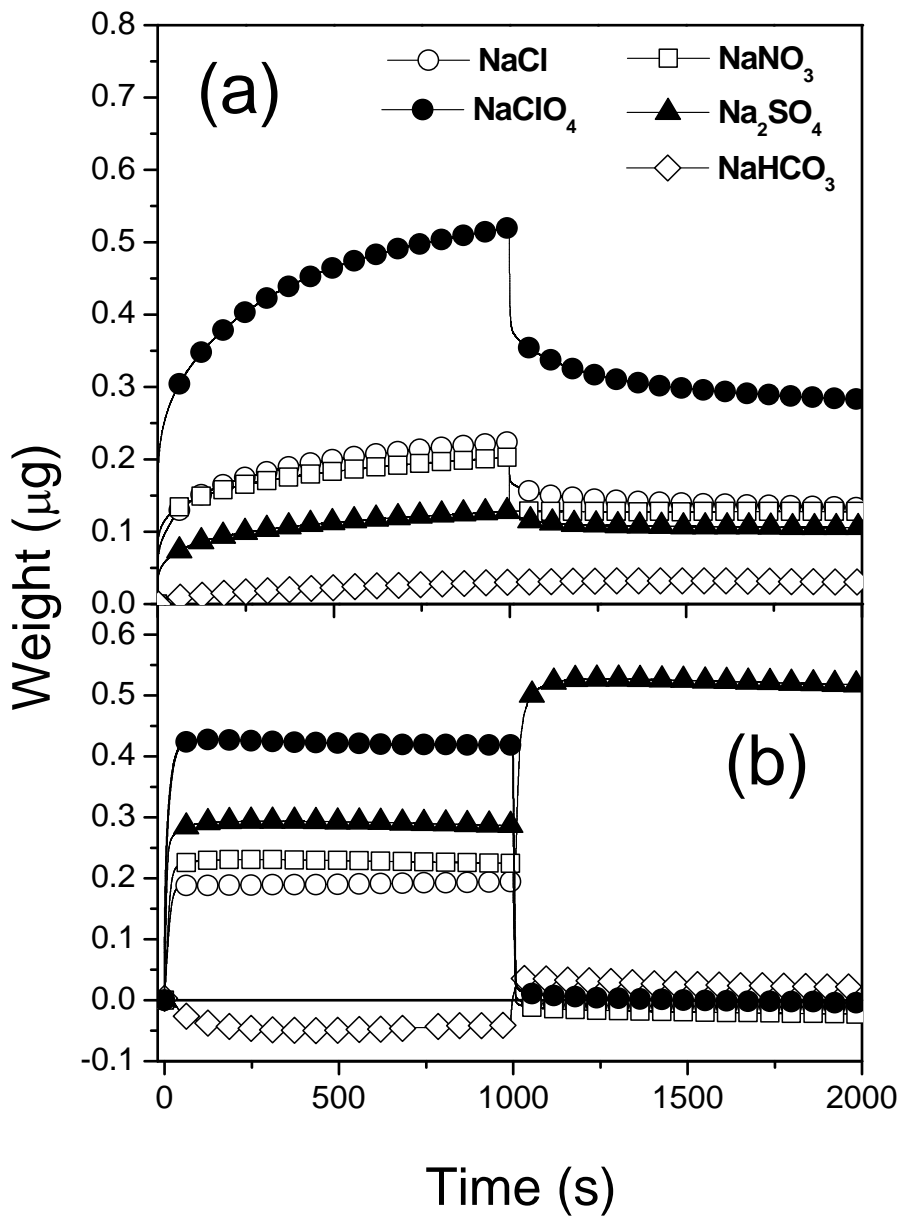


Figure 12. Chronoamperometry-EQCM Plot of (a) PPy (0.4V and 0V for 1000 s) and (b) CNT/PPy Composite (0.4 V and -0.8 V for 1000 s) in Different Electrolyte Solutions

Table 2. Anion Loading Capacity of PPy and CNT/PPy in Various Anions Containing Electrolyte in CV and Chronoamperometry Mode of EQCM

Mode		Cyclic Voltammetry				Chronoamperometry			
Electrode		PPy		CNT/PPy		PPy		CNT/PPy	
Anions	M.W.	Mass (ng)	Mole (%)	Mass (ng)	Mole (%)	Mass (ng)	Mole (%)	Mass (ng)	Mole (%)
Cl ⁻	35.5	147	11.0	175	13.1	224	16.8	201	15.1
ClO ₄ ⁻	99.5	396	10.6	402	10.7	519	13.9	419	11.2
NO ₃ ⁻	62.0	162	6.9	239	10.3	203	8.7	225	9.6
SO ₄ ²⁻	96.1	37	0.1	231	6.4	132	3.7	283	7.8
CO ₃ ²⁻	60.0	6	0	0	0	0	0	0	0

Mole %: mole of anion per mole of Py in PPy (PPy and CNT/PPy weight of 2.52 µg).

4.4 Development of a Laboratory-Scale ESIX Flow Reactor

4.4.1 PPY/CNT Nanocomposites and PPY/CNT/Carbon Fleece Composite Electrodes for ESIX Flow Reactor

PPY/CNT nanocomposites were prepared on the surface of a carbon fleece (CF) electrode for application in the ESIX flow reactor. To reduce the cost of the final flow reactor, a new, low-cost CF material (Sigratherm GFA10, SGL Carbon) was used to fabricate the flow reactor electrodes. CF is a porous conductive material, which is flexible for attaching the PPY/CNT nanocomposites. The preparation of the PPY/CNT nanocomposite was as follows. First, a CF electrode was pretreated with deionized water to facilitate wetting the hydrophobic carbon fibers by the aqueous solutions. Secondly, the CNT-DMF (5 mg/mL) solution was cast on the surface of the CF electrode and dried in air. Then, the PPY was electrodeposited on the surface of the CNT-modified, CF electrode in a Py solution for 10 min at an applied potential of 0.8 V. Finally, the ion exchanger electrode was washed with deionized water and dried in air. Figure 13 shows SEM images (with both low and high magnification) of CF (A, B), CNT-CF nanocomposites (C, D), and PPY/CNT-CF nanocomposites (E, F). A porous and homogeneous polymer covers the surface of the CNT-modified CF.

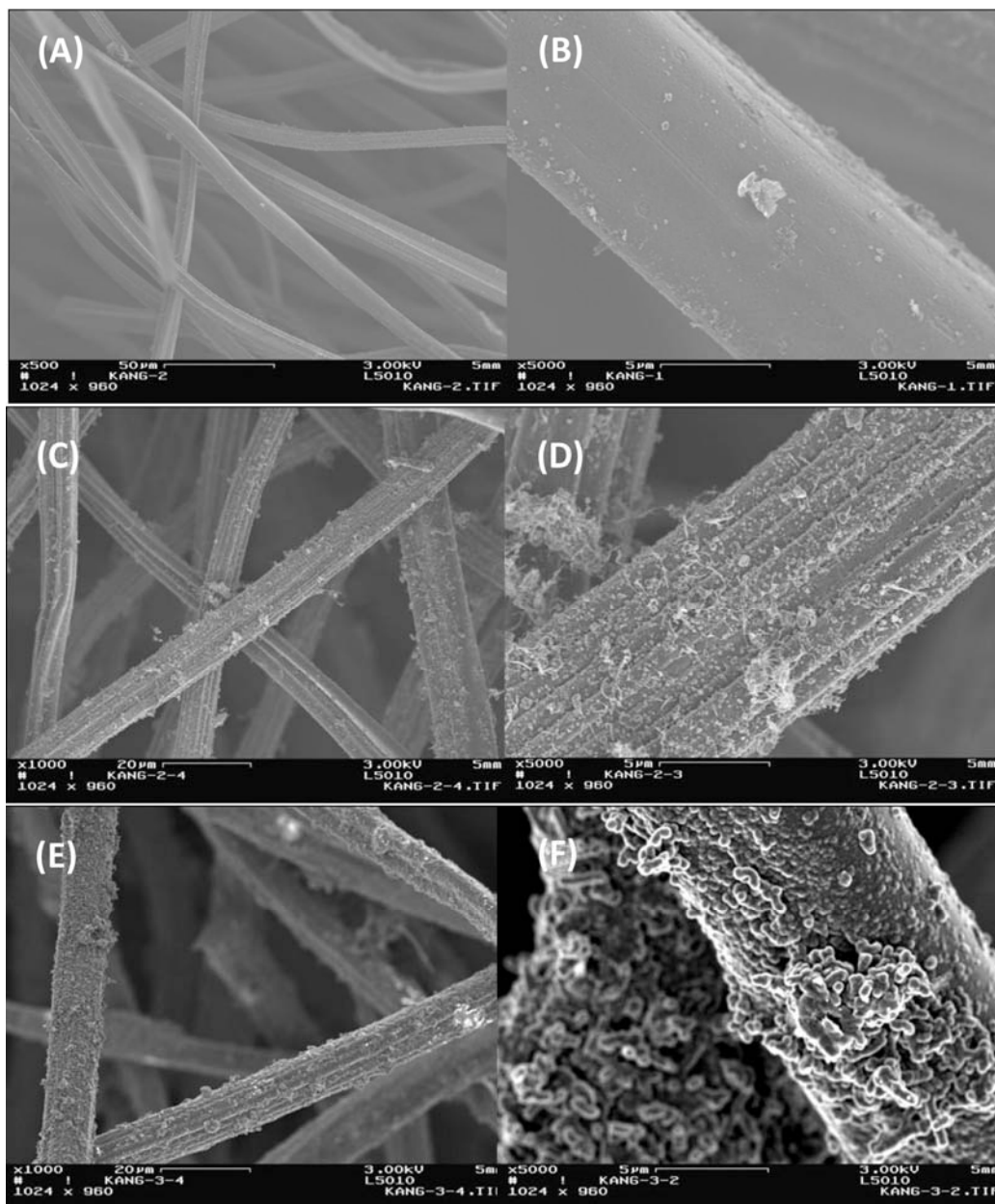


Figure 13. SEM of the CF (A, B), CNT-Modified CF (CNT-CF) (C, D), and Electrochemically Deposited PPy on CNT-CF (PPy/CNT-CF) (E, F)

4.4.2 Test of the Ion Exchange Electrodes

We first optimized the electrochemical deposition time of PPy on CNT-CF electrodes. The results show that a 20-min electrodeposition is the best (seen from the CVs in Figure 14-A). And then we studied the reduction-oxidation cycling stability of PPy films (Figure 14 2-B). The peak of the oxidation current for PPy/CNT-CF is higher than that of PPy/CF. The stability of PPy films on the porous CNT matrix has been improved greatly. The three-dimensional structure of

the nanocomposity may have improved the ion exchange capacity and the stability of the CNT/PPy film.

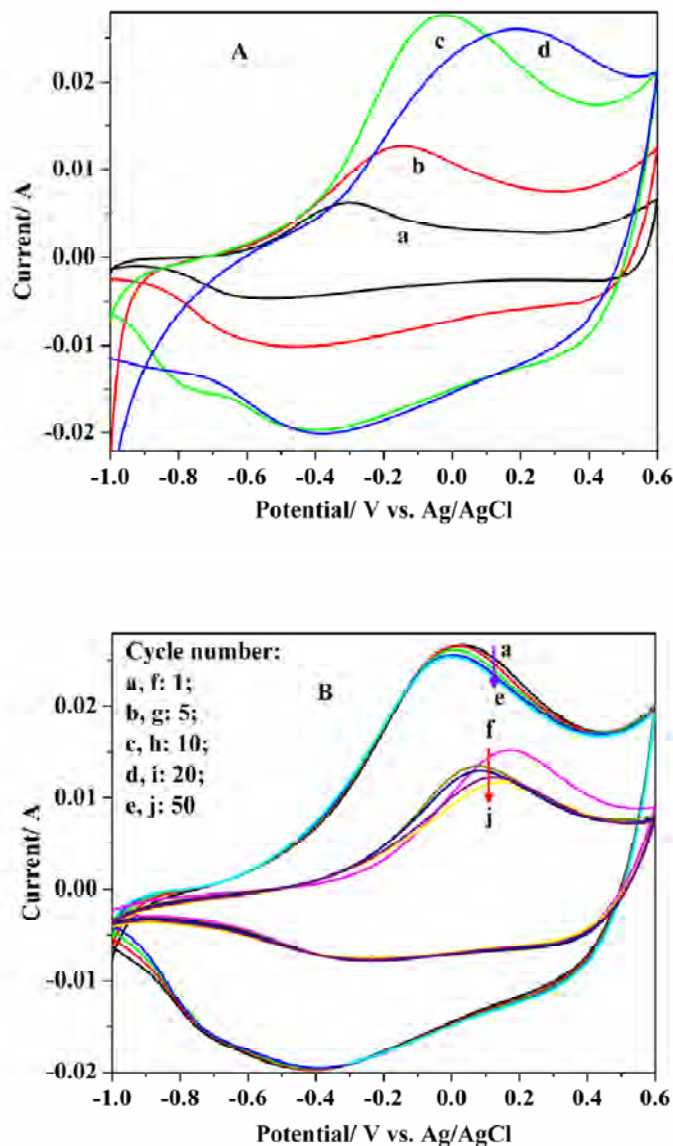


Figure 14. (A) CVs of the PPY/CNT-CF Electrodes in 0.5 M ClO_4^- Solution with Different Deposition Times (a-d): 5, 10, 20, and 30 min; (B) Consecutive CVs of PPY/CNT-CF Electrode (a-e), and PPY/CF (f-j) Electrode in 0.5 M ClO_4^- Solution. The cycle numbers of 1, 5, 10, 20, and 50 are shown. The scan rate was 5 mV/s.

We studied the selectivity of PPY/CNT-CF electrodes towards ClO_4^- , NO_3^- , and Cl^- anions. The crystallographic radii of these anions are somewhat different: ClO_4^- (0.240 nm), Cl^- (0.181 nm) and NO_3^- (0.129 nm). The shape of these anions is also remarkably different: the perchlorate is a tetrahedral, the nitrate is planar, and the chloride ion is a spherical anion. Obviously, such differences should have some influence on their strength of interaction with polymer chains and

also on their mobility in the polymer films. This PPy/CNT-CF is better for ESIX of perchlorate than nitrate and chloride ions (Figure 15-A). The Epox is in the following sequence—perchlorate (-86.1 mV) < nitrate (66.7 mV) < chloride (118.9 mV)—which indicates that perchlorate is much easier for ESIX because of its good affinity in the PPy/CNT-CF nanocomposite. Figure 15-B displays the cyclic voltammograms of a PPy/CNT-CF electrode in different concentrations of NaClO₄. The Epox shifts toward lower potentials as the concentration of NaClO₄ increases. This results in a negative slope when the oxidation peak potentials are plotted against Log(ClO₄⁻) (Epox = -0.0993-0.0626 log[ClO₄⁻], Figure 15-C), in which the slope (0.0626) obtained for ClO₄⁻ is close to the ideal Nernstian value (0.059). These results confirm that the PPy oxidation is mainly governed by the insertion of perchlorate.

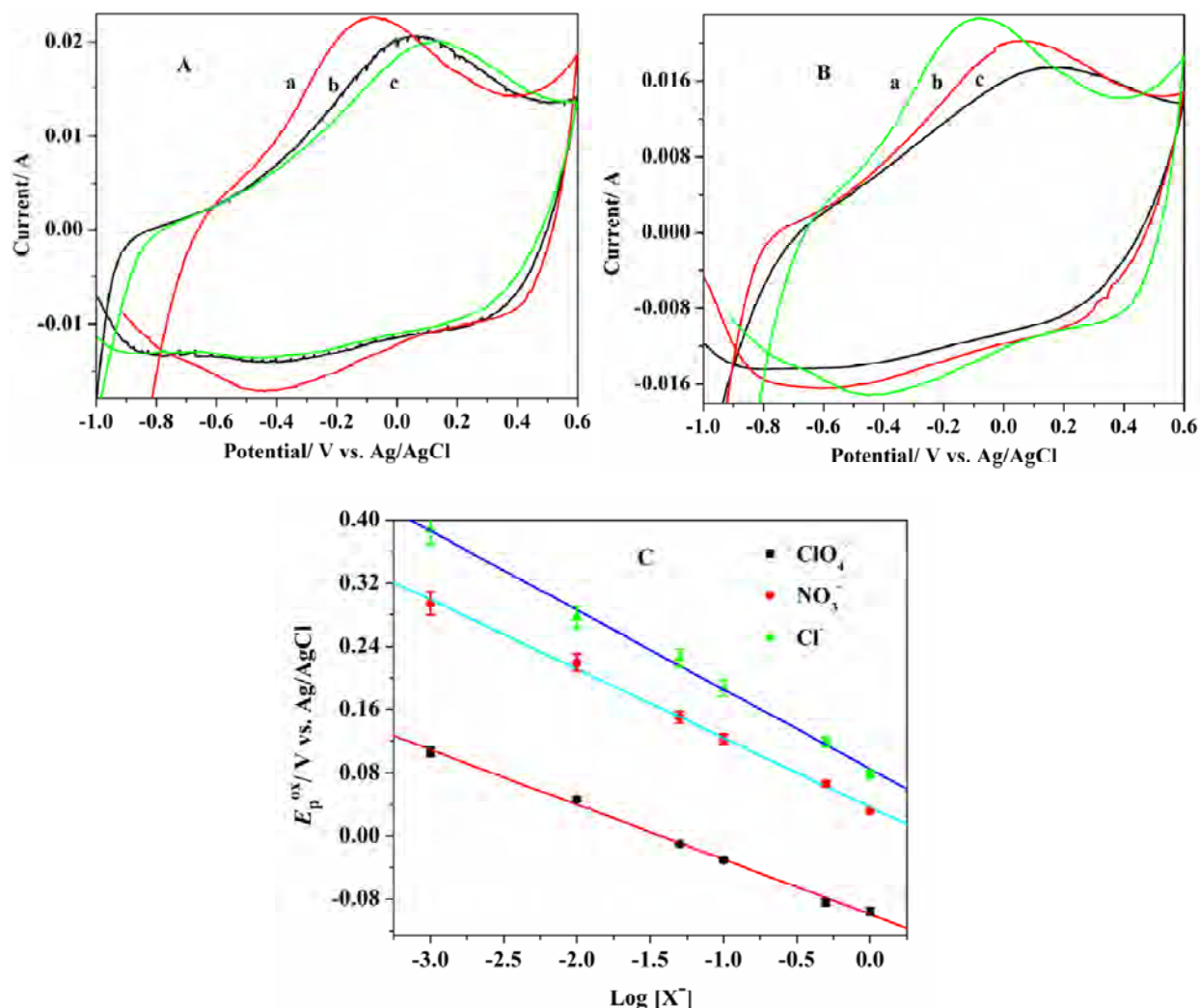


Figure 15. (A) CVs of the CF-CNT-PPy Electrode in Various Solutions of (a) ClO₄⁻, (b) NO₃⁻, and (c) Cl⁻ (0.5 M); (B) CVs of the CF-CNT-PPy Electrode in Different Concentrations of ClO₄⁻ (a-c): 0.5, 0.01 and 0.001 M; (C) Epox as a Function of Log (X); the Scan Rate was 5 mV/s

XPS was used to provide more information on the composition of the CF-CNT-PPy film after the electrically switched anion exchange. Figure 16 shows the high-resolution, XPS Cl spectra. The relative intensity of ClO_4^- and Cl^- in the XPS spectra indicates that perchlorate has been taken into the PPy/CNT-CF film, and most of the chloride ions have been taken out from the film. After the CF-CNT-PPy electrode was applied, there was a potential at 0.5 V for 400 s in 0.1-M ClO_4^- solution and then at -0.8 V for 400 s in 0.1-M NaCl solution. Then the peaks of ClO_4^- became smaller. The fact that the CF-CNT-PPy electrode is at 0.5 V for 400 s in 0.1 M ClO_4^- with a 0.5 M NO_3^- solution (Figure 16e) shows that the peaks of ClO_4^- became the same as those in Figure 16d, which means that perchlorate has a better affinity in the nanocomposite of CNT-PPy than nitrate, indicating a high selectivity for perchlorate.

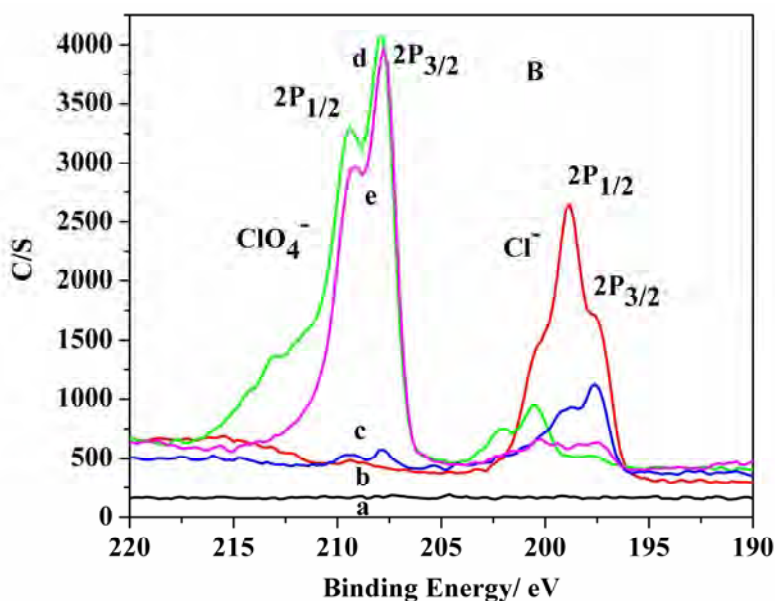


Figure 16. High Resolution XPS Cl Spectra for CNT-CF (a, control foam), and PPy/CNT-CF Film Prepared in Different Processes; (b) in 0.1 M Py Solution with 0.1 M NaCl at 0.8 V for 20 min; (c) at 0.5 V for 400 s in 0.1 M ClO_4^- Solution and then at -0.8 V for 10 Min in 0.1 M NaCl Solution; (d) at 0.5 V for 400 s in 0.1 M ClO_4^- Solution; (e) at 0.5 V for 400 s in 0.1 M ClO_4^- with 0.5 M NO_3^- Solution

4.4.3 Flow Reactor Fabrication and Optimization

Two ion exchanger electrodes ($4\text{ cm} \times 4\text{ cm} \times 1\text{ cm}$) separated by an ion-exchange membrane were assembled in a two-compartment cell to investigate the applicability of PPy/CNT ion exchange electrodes for continuous operation (Figure 17). The ion exchange electrodes were connected to two potentiostats. The continuous process is alternately controlled by potentiostat-1 and -2. To avoid over-oxidation of the PPy, the oxidation of the ion exchange working electrode is controlled potentiostatically during regeneration, while the other ion exchange electrode operates as a counter-electrode. For example, during regeneration in cell 1, the ion exchanger electrode is connected to potentiostat-1 as the working electrode WE1 versus the reference electrode RE1, and the electrode in cell 2 operates as counter-electrode CE1. During regeneration in cell 2, the electrode is connected to potentiostat-2 as working electrode WE2, and

its potential is controlled versus reference electrode RE2 while the electrode in cell 1 operates as counter-electrode CE2. To test this assembly, a perchlorate solution was continuously pumped through cell 1.

The flow reactors are first characterized with high-concentration perchlorate solution and then are used to test the low-concentration perchlorate solution, which mimics the contaminated groundwater.

The flow reactor testing includes the removal efficiency for perchlorate, selectivity, and loading capacity.

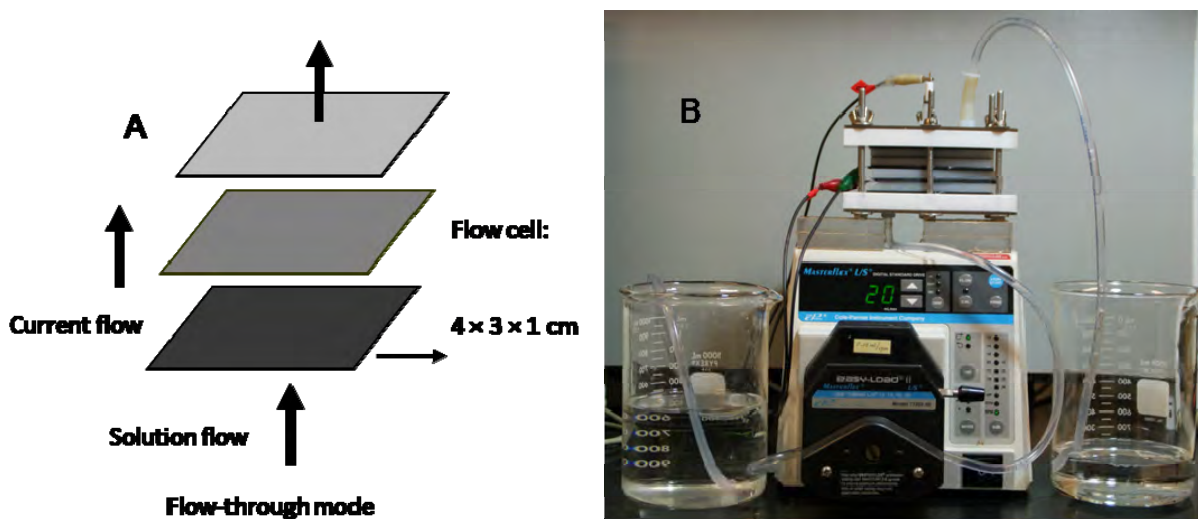


Figure 17. (A) Scheme of Solution and Current Flow in Electrochemical Cell Used for Flow Tests; (B) Micro Flow Cell Apparatus. This flow reactor consists of three electrodes and plastic material for stacking and insulating the electrode and sample delivery system, which consists of a pump, valves, and tubing.

Perchlorate Removal Efficiency of the Flow Reactor

The removal efficiency of perchlorate was studied in the condition of applied potentials and different flow rates. We found that the saturation capacity of perchlorate loading for the CF-CNT-PPy electrode (about 55%) is much higher than that for the CF-PPy electrode (30%), indicating that the effective loading area of CF-CNT-PPy is larger than that of CF-PPy. When the CF-CNT-PPy electrode was applied with a potential of 0.5 V, the removal efficiency was close to 80% for 10 hours. The result shows that PPy film on the surface of the CF-CNTs has a high affinity to perchlorate at an applied potential (0.5 V). The removal efficiency of the reactor for perchlorate is under 20% at the initial time for mixing the solution of perchlorate (0.1 mM) and nitrate (10 mM). However, the removal efficiency was almost 80% after 15 hours (Figure 18).

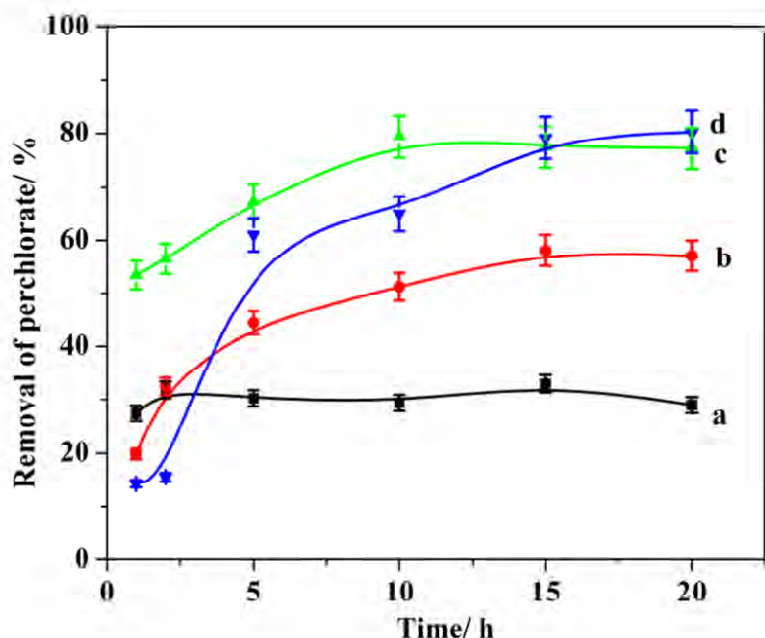


Figure 18. Removal of Perchlorate for the Continuous Process in Different Conditions: (a) CF-PPy Electrode; (b) CF-CNT-PPy Electrode; (c) CF-CNT-PPy Electrode Potentiostatically Controlled at 0.5 V in Perchlorate Solution (0.1 mM); and (d) CF-CNT-PPy Electrode Potentiostatically Controlled at 0.5 V in the Mixed Solution of Perchlorate (0.1 mM) and Nitrate (10 mM) at a Flow Rate of 10 mL/min

We found that the removal efficiency of the flow reactor for perchlorate was influenced by flow rates and the applied potential (Figure 19). The removal efficiency decreased as the flow rate increased. A flow rate of 10 mL/min was used in the experiments. As the applied potential increases, the removal efficiency for perchlorate increases. An optimum range of absorption potential of 0.5 and 0.6 V can be taken here for the present set of experiments.

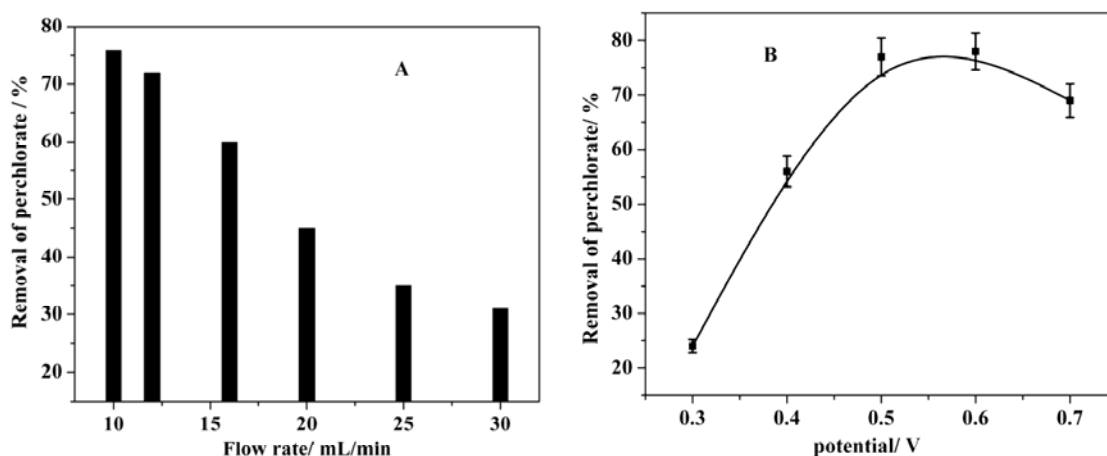


Figure 19. (A) Removal of Perchlorate for CF-CNT-PPy Film in Perchlorate Solution (0.1 mM) at Different Flow Rates; (B) at a Different Applied Potential with a Continuous Flow Rate of 10 mL/min for 10 Hours

The Selectivity of the Flow Reactor for Perchlorate Removal

The selectivity of the CF-CNT-PPy electrode in the flow reactor was investigated by XPS at different conditions (Figure 20). The CF-CNT-PPy electrode shows good selectivity to perchlorate. From the XPS data, the selectivity of the CF-CNT-PPy electrode for perchlorate over NO_3^- and Cl^- with a ratio of 1:100:100 (ClO_4^- : NO_3^- : Cl^-) is 120 and 353, respectively.

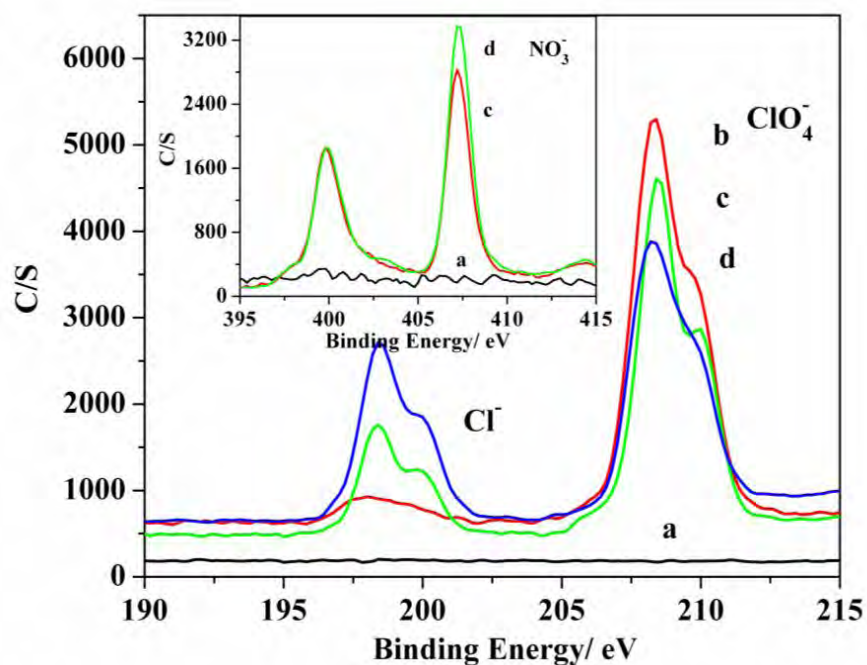


Figure 20. High-Resolution Cl Spectrum for the Film of the CF-CNT (a, control foam) Electrode and the CF-CNT-PPy Electrode at 0.5 V for 15 hours in 0.1 mM ClO_4^- Solution (b); in 0.1 mM ClO_4^- with 1.0 mM NO_3^- and Cl^- Solution (1:10:10, c), and with 10 mM NO_3^- and Cl^- Solution (1:100:100, d); Inset is the High Resolution N Spectrum, at a Flow Rate of 10 mL/Min

The Loading Capacity of the Flow Reactor

The loading capacity of the flow reactor was investigated at a condition of the 1.0 ppm perchlorate concentration (C_0) and a flow rate of 10 mL/min (12 BV/h). The bed volume (BV) of the flow cell is about 50 mL. C is the perchlorate concentration that stays in the solution past the separate electrode. No breakthrough was observed until 240 BV. When the 1.0-ppm perchlorate solution mixed with 100 ppm NO_3^- , Cl^- , CO_3^{2-} , and SO_4^{2-} flowing in the cell, no breakthrough was observed until 180 BV, and 50% breakthrough occurred at 280 BV. The results indicate that the flow reactor is selective in its efficiency for removing perchlorate from wastewater.

The Reusability of the ESIX

To test the reusability of the ESIX, the regeneration test of the CF-CNT-PPy electrode revealed that the capacity of the adsorbed perchlorate can retain above 80% of the first used uptake for 30 times of regeneration. After 50 times of regeneration, the CF-CNT-PPy films can uptake perchlorate above 70%, which indicates that it is a quick and effective *in situ* regeneration process for the perchlorate affinity film.

5. Conclusions

This research has demonstrated the viability of ESIX for perchlorate separations. Ion loading and unloading are easily controlled by modulating the electrode potential. Compared with conventional ion-exchange processes, the use of a regenerable material and the minimization of secondary waste are significant advantages in favor of the ESIX process.

The specific findings obtained from this SERDP-funded research include:

- Developed a direct electrochemical approach to synthesize PPy/CNT nano-composites.
- Demonstrated the feasibility of a PPy/CNT nano-composite for removing perchlorate from aqueous solutions through electrically switched anion exchange.
- Demonstrated that the PPy/CNT nano-composite exhibits a higher anion exchange capacity, cycling stability, loading/unloading reversibility, and selectivity for ClO_4^- uptake and elution than the PPy membrane.
- Demonstrated the feasibility of PPy/CNT nano-composite in a flow reactor for removing perchlorate from aqueous solutions through electrically switched anion exchange.
- Demonstrated that the PPy/CNT nano-composite exhibits a higher anion exchange capacity, loading/unloading reversibility, and selectivity for ClO_4^- uptake and elution than the PPy membrane.
- Demonstrated that the technology is ready for scale-up testing with the integration of multiple-flow reactors.

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Attachment 1: Publications and Presentations

1. Lin, Y.; Choi, D.; Wang, J.; Bontha, J. R., "Nanomaterials-Enhanced Electrically Switched Ion Exchange Process for Water Treatment." Chapter 14 in *Nanotechnology Applications for Clean Water*, ed. M. Savage, et al., pp. 179–189. William Andrew, Norwich, NY (2009).
2. Zhang, S.; Shao, Y.; Liu, J.; Aksay, I. A.; Lin, Y., Highly efficient and low cost graphene-based nanocomposite for water purification, **2010**, In Preparation.
3. Kang, X.; Shao, Y.; Wang, J.; Wu, H.; Lin, Y., A green and in situ regeneration process for perchlorate removal based on electrically switched ion exchange and nanocomposites, **2010**, In Preparation.
4. Choi, D.; Wang, J.; Engelhard, M.H.; Lin, Y, Electrochemically-Switchable Ion-exchange Property of Carbon Nanotubes/Polypyrrole Nanocomposite in Various Electrolyte Solutions, **2010**, In Preparation.
5. Lin, Y., Cui X.; Bontha, J., Electrically Controlled Anion Exchange Based on Polypyrrole/Carbon Nanotubes Nanocomposite for Perchlorate Removal. *Environmental Science & Technology*. **2006**, 40, (12), 4004-4009.
6. Cui, X., Engelhard, M. H.; Lin, Y, Preparation, Characterization and Anion Exchange Properties of Polypyrrole/Carbon Nanotube Nanocomposite. *Journal of Nanoscience and Nanotechnology* **2006**, 6, (2), 547-553.
7. Lin, Y.; Cui, X., Electrosynthesis, Characterization, and Application of Novel Hybrid Materials Based on Carbon Nanotube-Polyaniline-Nickel Hexacyanoferrate Nanocomposites. *Journal of Materials Chemistry*. **2006**, 16, (6), 585-592.
8. Lin, Y.; Cui, X., Novel Hybrid Materials with High Stability for Electrically Switched Ion Exchange: Carbon Nanotubes/Polyaniline/Nickel Hexacyanoferrate Nanocomposites. *Chemical Communications* **2005**, 17, 2226-2228.
9. Bontha, J.; Lin, Y.; Cui, X., "Novel Electrochemical Process for Treatment of Perchlorate in Waste Water." Presented at *Partners in Environmental Technology Technical Symposium*, sponsored by SERDP and ESTCP; Washington, DC (November 29-December 1, 2005).
10. Lin, Y.; Bontha, J.; Wang, J., "Novel Electrochemical Process for Treatment of Perchlorate in Waste Water." Presented at *Partners in Environmental Technology Technical Symposium*, sponsored by SERDP and ESTCP; Washington, DC (November 28-30, 2006).
11. Lin, Y.; Bontha, J.; Choi, D.; Wang, J., "Novel Electrochemical Process for Treatment of Perchlorate in Waste Water." Presented at *Partners in Environmental Technology Technical Symposium*, sponsored by SERDP and ESTCP; Washington, DC (2007).
12. Lin, Y.; Bontha, J.; Kang, X.; Wang, J., "Novel Electrochemical Process for Treatment of Perchlorate in Waste Water." Presented at *Partners in Environmental Technology Technical Symposium*, sponsored by SERDP and ESTCP; Washington, DC (2008).
13. Lin, Y.; Bontha, J.; Kang, X.; Wang, J., "Novel Electrochemical Process for Treatment of Perchlorate in Waste Water." Presented at *Partners in Environmental Technology Technical Symposium*, sponsored by SERDP and ESTCP; Washington, DC (2009).