



# A new interpretation of electrochemical impedance spectroscopy to measure accurate doping levels for conducting polymers: Separating Faradaic and capacitive currents

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## ABSTRACT

We report an electrochemical impedance spectroscopy (EIS) based method to measure the doping level of conducting polymers. Using EIS the Faradaic current and the capacitive charging current can be separated without relying on any unverifiable assumptions. We demonstrate the method for three types of conducting polymer thin films that are the basis for many commercial applications (poly(3,4-ethylenedioxythiophene), poly-3-hexylthiophene and polypyrrole).

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## 1. Introduction

Conducting polymers first attracted attention with the experimental demonstration of metallic conductivity in polyacetylene by Macdiarmid [1]. While the air instability of polyacetylene makes it an unattractive candidate for practical device applications, a number of air stable conducting polymers have since been synthesized and characterized in great detail [2]. They have proven useful for device applications because they are electronic materials that can be inexpensively synthesized and processed to meet specific performance needs. Air stable conducting polymers have been used as both semiconducting active materials and as metallic contact electrodes due to their tunable (both electrochemically and chemically) electronic properties, and low cost (and relative ease) of fabrication compared to the traditional inorganic semiconductors and metals [3]. Furthermore, the highly tunable optical properties of conducting polymers allow for a number of applications including electrochromic displays [4], and solar cells [2].

The critical parameter in determining the conductivity and the color of conducting polymers is the level of oxidation or the doping level [5]. As the polymer becomes oxidized, the overall film

conductivity increases (up to a certain level and starts decreasing with overoxidation) and optical absorption properties change (both wavelength and strength of the absorption [6]). Accurate knowledge of doping levels is crucial for a precise description of the electronic properties, and the changes thereof, of these materials (therefore also important for practical devices such as polymer Li ion batteries, organic light emitting diodes (OLEDs) and organic thin films transistors (OTFTs)). Even though specific methods to quantify the doping level of conducting polymers have been documented, they are either restricted to polymers doped with a specific oxidant (Fe(III) for Mössbauer Spectroscopy [7]), or inaccurate in some way (poor knowledge of film swelling and solvation numbers of counter ions in Electrochemical Quartz Crystal Microbalance) [8]. To our knowledge, no accurate universal method for measuring the doping levels of conducting polymers has been established to date.

One commonly employed method of estimating the doping level is to integrate the charge under the cyclic voltammetric profile without any explicit reference to the change in the capacitive charging current. In cyclic voltammetry, in general, current flows through two separate mechanisms. First, there is the current related to the charge needed to change the oxidation state of the electroactive molecules (Faradaic current), and second there is the current that accounts for the charge needed to change the charge state of the “double layer” type capacitors on the various interfaces within the cell (capacitive currents). Since the capacitive part of the current has no contribution to the oxidation state, one needs to separate the capacitive component and integrate the

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Faradaic component in order to measure changes in the oxidation state (doping level). A simple baseline subtraction of the current when the Faradaic current is zero (i.e. at potentials where no oxidation or reduction takes place) is appropriate for most experiments, however for conducting polymer films on electrodes, this method may greatly overestimate the doping level because the capacitance and thus the capacitive charging current are not constant throughout the sweep. The capacitance increases throughout an oxidative sweep for two reasons. First, because the polymer becomes more conductive as it is oxidized, the dielectric constant of the polymer increases. Second, the solvent and counter-ion molecules that get drawn into the polymer film during oxidation cause swelling. This increases the surface area of the film, leading to an increased “double layer” capacitance. Because of these two reasons, the capacitance of a conducting polymer film can vary by many orders of magnitude during cyclic voltammetric experiments, making it essentially impossible to determine the fraction of the total current that is Faradaic in nature and precluding an accurate measurement of the doping level.

We present an electrochemical impedance spectroscopy (EIS) [9] based method of separating the capacitive charging current involved in the oxidation process. Our method uses parameters obtained through the conventional EIS measurements and calculates the ratio of the capacitive current that flows in a cyclic voltammetry experiment to the total current through a straightforward circuit analysis of the model circuit employed in the EIS data analysis. The method enables us to accurately distinguish the capacitive current, allowing us to calculate the doping level at the potentials of interest. This method is superior to the previously mentioned ones because it measures the film properties directly rather than relying on unverifiable assumptions about the film capacitance or the number of solvent molecules accompanying the counter ions.

## 2. Experimental

Propylene carbonate (HPLC grade, Aldrich), trichloroethylene (98%, JT Baker), tetrabutylammonium perchlorate (99%, Aldrich), poly-3-hexythiophene (P3HT) (Aldrich, 99% regioregular), polypyrrole (PPy)(Aldrich, doped 10–40 S/cm) [10] and 3,4-ethylenedioxythiophene (EDOT, Baytron M, Bayer Co., Germany) were used as received. Poly(3,4-ethylenedioxythiophene) (PEDOT) was chemically prepared from EDOT monomer using  $\text{Cu}(\text{BF}_4)_2$  as an oxidizing agent. 14.2 g (0.1 mol) of EDOT were dissolved in 200 ml of anhydrous acetonitrile. 200 ml of acetonitrile solution containing 47.4 g (0.2 mol) of  $\text{Cu}(\text{BF}_4)_2$  were added dropwise to the EDOT monomer solution and stirred for 24 h at room temperature under an argon atmosphere. The dark blue precipitate obtained was then filtered, washed with  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and acetone, and dried under vacuum for 72 h.

The impedance data, as well as the cyclic voltammograms were recorded on a Solartron 1280B using ZPlot and Corrware as recording software. The impedance data were recorded from 10 kHz to 0.05 Hz with logarithmic sampling with 15 points per decade. After stepping the potential to a given value, the impedance measurement started after the current was below 10 nA (about 5 min for our films) which ensured that the polymer film was equilibrated at that potential.

Fitting of the data was performed using a complex non-linear least squares algorithm using ZView 2.8d without any weighting of the data.

The films were prepared using a suspension of ~10 mg of the appropriate polymer in 2 ml of trichloroethylene. The suspension was sonicated for 15 min before every use. Using a microliter syringe, a 2  $\mu\text{l}$  drop of the suspension was placed carefully on just the glassy carbon surface and the solvent was evaporated under vacuum for 2 h.

We used a 3 mm glassy carbon electrode sealed in Teflon with a copper wire embedded in tightly pressed carbon felt used to make electrical contact from the back. In this way the DC contact resistance from the surface of the glassy carbon to the copper wire was less than 1  $\Omega$ . The glassy carbon electrode was cleaned by cycling the potential in 0.1 M NaOH solution between 0 and 1.4 V vs. Ag/AgCl until the oxidative current at the positive end of the sweep disappeared and the sweep was reproducible.

The impedance spectroscopy data were obtained using a three electrode cell with a Ag/AgCl reference electrode and a Pt coil counter electrode.

## 3. Methodology

Our method makes extensive use of the well documented method of EIS [9]. In EIS analysis, impedance data taken at a number of frequencies are fit to a model circuit to determine the parameters for each element of the circuit at a fixed potential. Once the parameters are obtained, we calculate the ratio of Faradaic and capacitive currents to the total current through a simple circuit analysis at the potentials where we performed EIS. Finally, we integrate the Faradaic current to determine the doping level of the polymer.

The circuit model we use is depicted in Fig. 1. It is adapted from Lyons [11] with a slight modification (the model used in Lyons used a capacitor where we are using a constant phase element— $\text{CPE}_{\text{film}}$ ) to accommodate the roughness [9] in the interface between the electrode and the polymer film due to our use of a glassy carbon electrode. The circuit consists of two parts: one modeling the bulk film and the other modeling the film–solution interface. The part that models the film has two “arms” in parallel. The first “arm” contains a constant phase element and a resistor that represents the capacitive charging of the film. The other “arm” is a Warburg impedance that represents the Faradaic component. The part that models the film–solution interface includes a resistor representing the ion transfer resistance and a capacitor representing the double layer charging on the surface of the film.

Once the fitting was completed, we used the parameters of the circuit elements to calculate the ratio of the Faradaic current ( $I_f$ ) to total current (i.e. the ratio of the current going through the arm with the Warburg impedance to the arm with a constant phase element and a resistor). Given that  $R_{\text{film}}$  and  $\text{CPE}_{\text{film}}$  are in series to one another and in parallel to  $W_{\text{film}}$ , the impedance of the film can be expressed as:

$$\frac{1}{Z_{\text{film}}} = \frac{1}{R_{\text{film}} + Z_{\text{CPE}_{\text{film}}}} + \frac{1}{Z_{W_{\text{film}}}} \quad (1)$$

where  $Z_{\text{film}}$ ,  $Z_{R_{\text{film}}}$ ,  $Z_{\text{CPE}_{\text{film}}}$ , and  $Z_{W_{\text{film}}}$  represent the resultant film impedance, and the impedances of  $R_{\text{film}}$ ,  $\text{CPE}_{\text{film}}$ , and  $W_{\text{film}}$  elements, respectively. Since the potential drop across the film

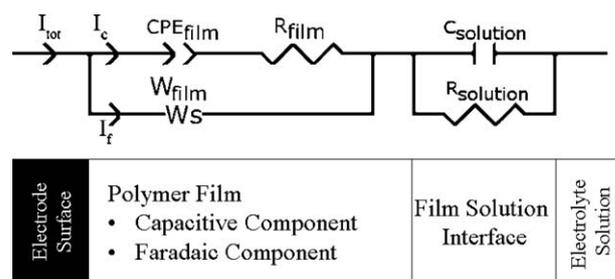


Fig. 1. The circuit model used in this study.  $I_f$  and  $I_{\text{tot}}$  denote Faradaic and total currents, respectively. Regions corresponding to the given circuit elements are denoted below the circuit diagram.

**Table 1**

Impedances of various circuit elements (see Barsoukov and Macdonald [9] for details on the definitions of the parameters).

	Impedance with respect to a sinusoidal voltage	Impedance with respect to voltage ramp
Capacitance	$1/i\omega C$	$t/C$
Constant phase element	$1/(i\omega)^P T$	$t^P/T$
Warburg impedance	$R \frac{\tanh((i\omega T)^P)}{(i\omega T)^P}$	$R \frac{\tanh((T/t)^P)}{(T/t)^P}$

must be equal to the product of the Faradaic current and the Warburg impedance as well as equal to the product of the total current through the film and the resultant film impedance, the ratio of the Faradaic current to the total current is given by

$$I_F \times Z_{W_{\text{film}}} = I_{\text{total}} \times Z_{\text{film}} \Rightarrow \frac{I_F}{I_{\text{total}}} = \frac{Z_{\text{film}}}{Z_{W_{\text{film}}}}$$

Substituting for the resultant film impedance:

$$\frac{I_F}{I_{\text{total}}} = \frac{((Z_{R_{\text{film}}} + Z_{CPE_{\text{film}}})^{-1} + Z_{W_{\text{film}}}^{-1})^{-1}}{Z_{W_{\text{film}}}} \quad (2)$$

Because the total current is equal to the sum of the Faradaic and capacitive currents, the ratio of the capacitive current to the total current can simply be calculated through  $1 - I_F/I_{\text{total}}$ .

Due to nature of impedance spectroscopy, all the circuit elements used are defined with respect to an oscillatory perturbation on the system. The analytical closed form expressions with respect to a sinusoidal wave are given in Table 1. In order to use these elements to calculate ratios in cyclic voltammetry, we must first define the impedances of the circuit elements with respect to a linear voltage ramp. To be able to do this, we start with the integrated form of Ohm's law which relates charge to potential. Then, we insert a linear voltage ramp ( $V = vt$ ) and solve for the

current as a function of potential. For example, the formula for a capacitor would be found in the following manner:

$$Q = CV, \quad V = vt \Rightarrow Q = Cvt$$

$$i = \frac{dQ}{dt} \Rightarrow i = Cv = \frac{CV}{t}$$

$$Z \equiv \frac{V}{i} \Rightarrow Z_C = \frac{t}{C}$$

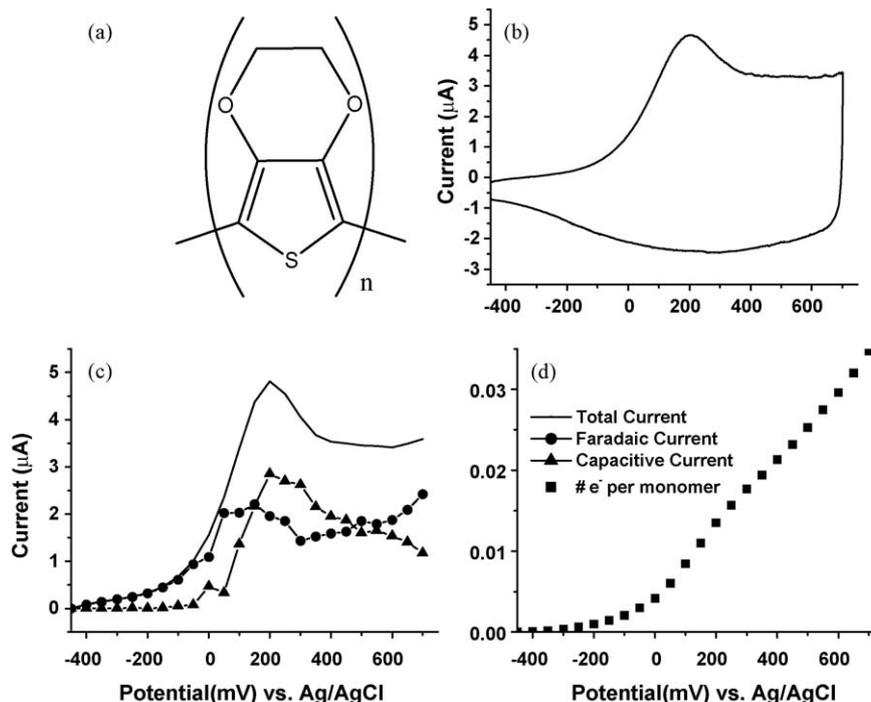
Similar analyses can be done for all the elements used in the circuit model. The results are summarized in Table 1. Once we have the appropriate form for the impedances, the calculation of the ratio of the Faradaic current to the total current is straightforward. The overall formula is given by

$$I_F/I_{\text{total}} = \frac{(((t^{P_{CPE_{\text{film}}}}/T_{CPE_{\text{film}}}) + R_{\text{film}})^{-1} + ((\tanh((T_{Z_{\text{diff}}}/t)^P)R_{Z_{\text{diff}}})/((T_{Z_{\text{diff}}}/t)^P)^{-1})^{-1}}{(\tanh((T_{Z_{\text{diff}}}/t)^P)R_{Z_{\text{diff}}})/((T_{Z_{\text{diff}}}/t)^P)} \quad (3)$$

where  $T_{CPE_{\text{film}}}$  and  $P_{CPE_{\text{film}}}$  are the modified capacitance and the exponent of the CPE<sub>film</sub> element,  $T_{Z_{\text{diff}}}$ ,  $R_{Z_{\text{diff}}}$  and  $P$  are the three parameters for the open circuit terminated Warburg element denoted  $Z_{\text{diff}}$ .  $T_{Z_{\text{diff}}}$  is a diffusion time constant related parameter modified by the exponent  $P$  and  $R_{Z_{\text{diff}}}$  is a resistance type parameter related to the diffusion constant. Further details can be found in Barsoukov and Macdonald [9]. Once this ratio is calculated, we can numerically integrate the Faradaic current within the cyclic voltammetric profile to get the Faradaic charge. This method enables us, for the first time, to separate Faradaic current from capacitive current, without any unverifiable assumptions. The only assumption in the method is the choice of a physically sensible circuit model, and that choice is verified by the fact that the fitting is excellent (fitting uncertainties of the EIS data to the model depicted in Fig. 1 is less than 3% for all the circuit elements).

The experimental process can be summarized in six steps:

1. Perform cyclic voltammetry at a slow enough rate for the film to be in electronic equilibrium with the applied potential.



**Fig. 2.** (a) Chemical structure of PEDOT, (b) CV at 10 mV/s, (c) current partitioning analysis, and (d) measured doping level of a dropcast film of PEDOT.

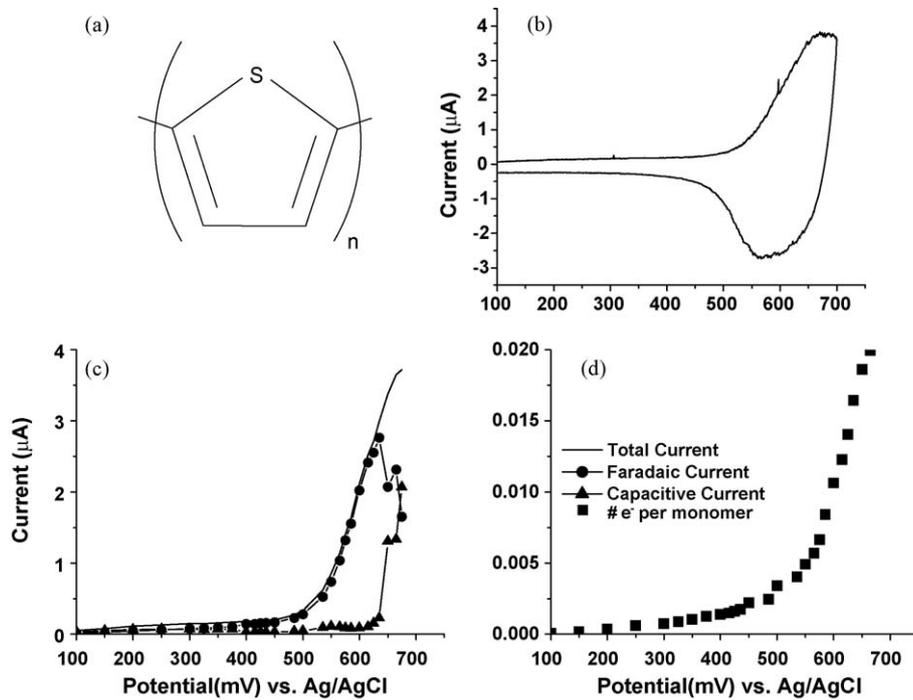


Fig. 3. (a) Chemical structure of P3HT, (b) CV at 10 mV/s, (c) current partitioning analysis, and (d) measured doping level of a dropcast film of P3HT.

- At selected constant electrochemical potentials, perform impedance spectroscopy (measure impedance when sweeping the frequency of the small amplitude AC excitation) at selected potentials after holding the potential constant for 5 min for the film to equilibrate at the given potential.
- Fit the impedance data using the circuit model given in Fig. 1.
- Calculate the ratio of Faradaic current to total current using Eq. (3).
- Multiply the ratio by the total current at selected potentials to obtain the Faradaic current.

- Perform numerical integration of the Faradaic current to obtain the Faradaic charge as a function of potential.

#### 4. Results and discussion

We apply our method to three different conducting polymers that are used in a number of applications: poly-3-hexylthiophene (P3HT), poly-3,4-ethylenedioxythiophene (PEDOT) and polypyrrole (PPy). We have chosen these polymers not only because of the commercial availability of pure and well characterized samples,

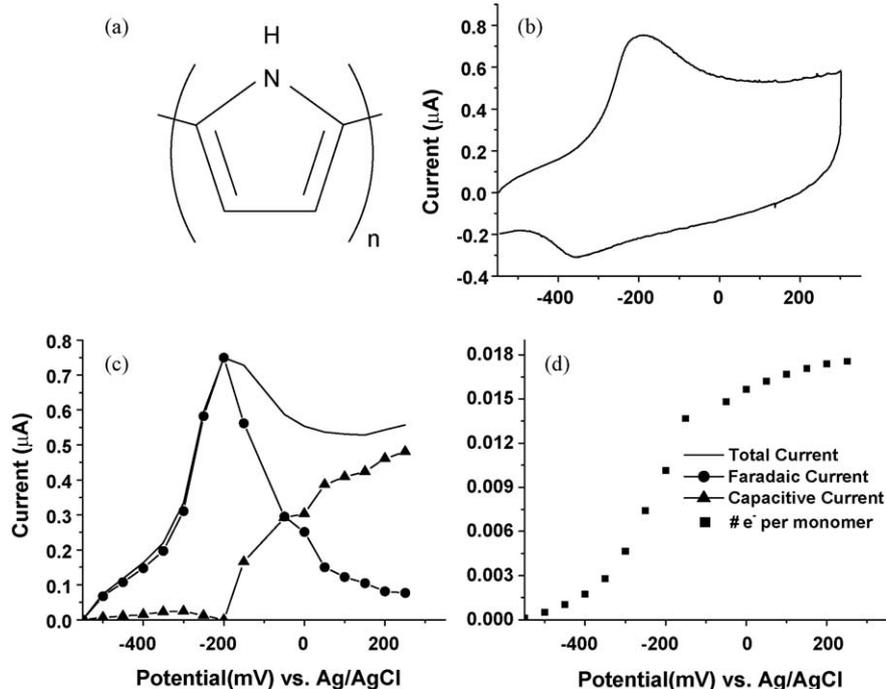


Fig. 4. (a) Chemical structure of PPy, (b) CV at 10 mV/s, (c) current partitioning analysis, and (d) measured doping level of a dropcast film of PPy.

and also because many polymers used in current commercial devices are derived from these basic materials.

The cyclic voltammetric profile of a dropcast film of PEDOT in 0.1 M TBAP in propylene carbonate at a sweep rate of 10 mV/s is shown in Fig. 2b. Focusing on the anodic sweep only, Fig. 2c presents the total current as well as the Faradaic and capacitive currents as calculated by the process presented above. The uncertainties in the current values are less than 2% at any given point. As seen in the figure, only a small fraction of the current is actually Faradaic. The charge resulting from the numerical integration is shown in Fig. 2d. The uncertainties are less than 3% at all potentials. As illustrated, the Faradaic charge required to bring the film to +700 mV from -450 mV (vs. Ag/AgCl) is less than half of the total charge.

The same analysis was done on dropcast films of P3HT (at a sweep rate of 10 mV/s) and PPy (at a sweep rate of 5 mV/s). The data are presented in Figs. 3 and 4 for P3HT and PPy, respectively. The uncertainties on the current values are less than 5% at all the points. The uncertainties on the charge values are less than 7%.

The similar behavior in the current profiles of the three polymers can be summarized as follows: at the more negative voltages, the Faradaic current increases as the oxidation process starts. As the polymer becomes oxidized, the capacitance and thus the capacitive current increases. At more positive potentials the Faradaic current decreases and the capacitive current remains constant because the capacitance of the conducting polymer film increases only as the polymer gets oxidized and the oxidation process only occurs at certain potentials (or decreases in the PEDOT case probably due to overoxidation as the Faradaic current seems to increase as well). The reason for the increasing capacitance can be explained as follows: The oxidized film is swollen, having a larger contact area with the solution and thus an increased double layer capacitance, in addition to a larger dielectric constant due largely to more charge carriers. Once the film is mostly oxidized, the Faradaic current decreases but never reaches zero over the potential window employed.

We suggest part of the reason that the Faradaic current never reaches zero is the fact that in a given film, there is a distribution of conjugation lengths. The redox potential of a particular part of the conducting polymer is related to the length of conjugation in that part. The longer the length of conjugation, the more stable the oxidized state, leading to more negative redox potential. Therefore, a distribution in the conjugation lengths directly translates to a distribution in oxidation potentials. On a given dropcast film, kinks and twists are highly likely to form at random positions on the chains. Because the extent of electronic states will be limited by these kinks and twists the lengths over which the doped states can extend will vary greatly across the film. This variation in conjugation length directly translates to a variation in oxidation potentials, resulting in a broad redox peak.

It should also be mentioned that the potential window over which these experiments can be done is considerably narrower than that of typical cyclic voltammetry experiments using the same materials. At the resolution and the integration times required for these experiments, we have to hold the electrochemical potential at specified values for about an hour, whereas in cyclic voltammetry this time is of the order of seconds. While conducting polymer films can survive highly oxidizing or highly reducing electrochemical potentials for seconds without adverse effects, they tend to degrade on the time scale of an hour, rendering them electroinactive. Therefore, the total number of electrons we measure even after integrating the total current is smaller by a factor of ~10–15 than those reported in the literature.

## 5. Conclusion

We have developed an EIS based method to calculate the doping levels of conducting polymers without any unverifiable assumptions. The technique relies on the measured impedance and a well documented circuit model [11] to fit the circuit parameters of the sample and then uses these parameters to separate the total current into its capacitive and Faradaic components. The separation allows accurate determination of doping levels of conducting polymers, which is an important parameter for both accurate theoretical explanations and for practical devices like Li ion batteries, OLEDs and OTFTs.

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## References

- [1] A.G. MacDiarmid, *Synth. Met.* 125 (2002) 11–22.
- [2] Skotheim, T.A., Elsenbaumer, R.L., Reynolds, J.R. (Eds.), *Handbook of Conducting Polymers*, second ed., Revised and Expanded, 2007, Marcel Dekker, NY.
- [3] J. Lu, N.J. Pinto, A.G. MacDiarmid, *J. Appl. Phys.* 92 (10) (2002) 6033.
- [4] R.J. Mortimer, A.L. Dyer, J.R. Reynolds, *Displays* 27 (2006) 2–18.
- [5] Both p-doping (oxidation) and n-doping (reduction) are possible for conducting polymers, yet p-doped, hole conductor conducting polymers are the more commonly studied variety. We will limit our discussion to oxidation (p-doping) but similar arguments are valid for reduction (n-doping).
- [6] G.R. Hutchison, M.A. Ratner, T.J. Marks, *J. Phys. Chem. B* 109 (2005) 3126–3138.
- [7] S. Kitao, M. Seto, Y. Maeda, T. Matsuyama, S. Masubuchi, S. Kazama, *J. Phys. Soc. Jpn.* 66 (4) (1997) 1195–1200.
- [8] G. Zotti, S. Zecchin, G. Schiavon, L.B. Groenendaal, *Chem. Mater.* 12 (2000) 2996.
- [9] E. Barsoukov, J.R. Macdonald, *Impedance Spectroscopy Theory, Experiment, and Applications*, second ed., Wiley-Interscience, 2005.
- [10] The molecular weight was obtained from Sigma Aldrich technical service, even though the exact structure and the amount of dopant is confidential information.
- [11] M.E.G. Lyons, in: M.E.G. Lyons (Ed.), *Electroactive Polymer Electrochemistry: Part 1*, Plenum Press, New York, 1994.