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### Study On The Electrochemical Doping Of Polyacetylene With Selected Metal Halides

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STUDY ON THE ELECTROCHEMICAL DOPING OF POLYACETYLENE WITH  
SELECTED METAL HALIDES

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Abstract Electrochemical oxidation has been found to be a convenient method for introduction of tetrachloride anions of Fe, Al, In, Tl into polyacetylene. EPR, Mössbauer spectroscopies and elemental analyses show that oxidation (doping) and reduction (undoping) cycle in  $(CH)_x - LiCl/MCl_3$  systems is not totally reversible - and is accompanied by irreversible side reactions which limit possible application of  $(CH)_x$  - metal chloride systems in energy storage devices.

INTRODUCTION

In our previous papers we have shown that it is possible to oxidize polyacetylene electrochemically in an electrolyte consisting of a mixture of LiCl and a proper metal trihalide (1), (2), (3). This discovery extends the range of systems potentially applicable to polyacetylene-based rechargeable batteries. In this communication we concentrate on the studies of the reversibility of the described electrochemical oxidation. In addition to standard electrochemical tests we have carried out spectroscopic (EPR, Mössbauer) studies of polyacetylene electrode in order to monitor irreversible side reactions occurring upon each doping-undoping cycle.

## EXPERIMENTAL

Electrochemical vacuum cell with two separated compartments was used for all electrochemical experiments. For the oxidation (doping) either constant current of 0.1–0.2 mA/mg  $(\text{CH})_x$  or constant potential of 0.7–1.0 V vs Ag/AgCl reference were applied. Reductions (undopings) of the oxidized  $(\text{CH})_x$  were performed first at constant current of 0.1 mA/mg  $(\text{CH})_x$  then at constant potential lowered stepwise from 0.3 V to the potential of pristine polyacetylene in the investigated solutions. After the doping-undoping cycle selected samples were subjected to elemental analysis, EPR and, in the case of iron chloride system, Mössbauer spectroscopy.

## RESULTS

Electrochemical oxidation of polyacetylene in  $\text{MCl}_3/\text{LiCl}/\text{nitromethane}$  solutions (where  $\text{M} = \text{Fe}, \text{Al}, \text{In}, \text{Tl}$ ) leads to the formation of highly conducting ( $500\text{--}900 \Omega^{-1} \text{ cm}^{-1}$ ) polymers. The observed current yields were high (80–90 %). In most solutions concomitant chemical doping was negligible except  $\text{LiCl}/\text{TlCl}_3$  one but even in that case it never exceeded  $y = 0.015$  under the conditions of the electrolysis. In accordance with our previous studies (1), (2), (3) was it found that the composition of the polymers can be expressed by the following general formula :  $\{\text{CH}(\text{MCl}_4)_y\}_x$  if  $y \leq 0.065$  for  $\text{FeCl}_4^-$  and  $\text{InCl}_4^-$  and  $y \leq 0.045$  for  $\text{TlCl}_4^-$ .

The experiments of undoping (reduction) were carried out for  $\{\text{CH}(\text{FeCl}_4)_y\}_x$ ,  $\{\text{CH}(\text{InCl}_4)_y\}_x$  and  $\{\text{CH}(\text{TlCl}_4)_y\}_x$  in the same electrolyte solutions as used for the oxidation (doping) of pristine  $(\text{CH})_x$ .

It was found that in the case of  $\{\text{CH}(\text{TlCl}_4)_y\}_x$  the removal of the dopant through electrochemical reduction was not possible. Similar reduction carried out for  $\{\text{CH}(\text{InCl}_4)_y\}_x$  led to the removal of ca. 70 % of the initial  $\text{InCl}_4^-$  content. The average current yield observed during undoping was 80–90 % however at first stages

of the reduction it exceeded 100 % suggesting that some chemical processes take place simultaneously with the electrochemical removal of  $\text{InCl}_4^-$ . The elemental analysis of the reduction product gave the following formula  $\{\text{CH}_{1.07}(\text{InCl}_{4.33})_{0.014}\}_x$   
 $\Sigma \% \text{ C, H, In, Cl} = 98.48$ .

In one experiment, designed to study the reversibility of the oxidation-reduction cycling, after each cycle the polyacetylene electrode was subjected to the mass change measurements and to EPR spectroscopy. It was found that after each ox-red cycle the sample recovers its symmetric shape but the width of the signal increases (Fig. 1A). The same trend could be seen in the percentage of the residual dopant (Fig. 1B).

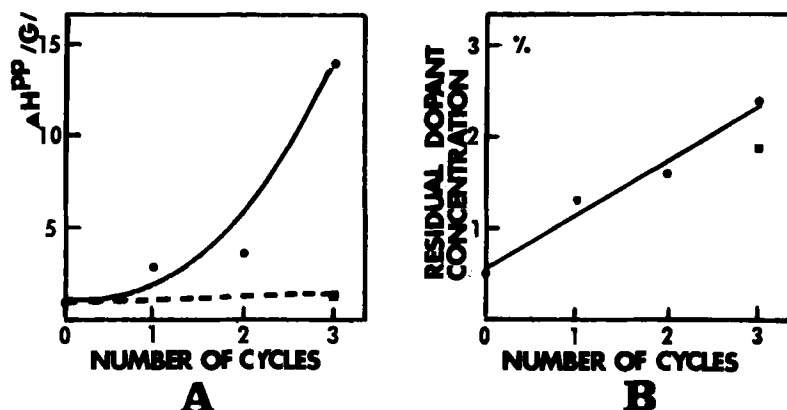


FIGURE 1 EPR and mass changes studies of polyacetylene electrode after doping-undoping cycles.  
 A -  $\Delta H_{PP}$  of polyacetylene after undoping.  
 B - Maximum dopant concentration at which EPR line is still symmetric ( $A/B$ ) = 1.

- - after each oxidation and reduction the sample was washed with pure solvent and vacuum dried before the mass changes and EPR measurements.
- - the sample was not washed and removed from the electrochemical cell between the cycles.

Similar phenomena can be observed upon electrochemical doping and undoping of polyacetylene in  $\text{LiCl}/\text{FeCl}_3/\text{nitromethane}$  systems. However since  $\text{FeCl}_4^-$  is paramagnetic an additional broad signal associated with its unpaired electrons is observed. The results of EPR and Mössbauer studies are summarized in Table 1. In the oxidation part of the ox-red cycle the intensity of the narrow signal characteristic of unpaired electrons in polyenic chains decreases. At  $\text{FeCl}_4^-$  concentration of 4.3 % the  $(\text{CH})_x$  signal becomes invisible. On the undoping (reduction part of the cycle) the reversed trend is observed but the broad signal returns to its symmetric shape at the residual dopant concentration of 2.0 % ie. higher than the onset of the signal assymetry in the oxidation part (0.5 %). In addition after the ox-red cycle the intensity of the narrow line is much smaller. Similarly as in the case of  $(\text{CH})_x$ - $\text{InCl}_3/\text{LiCl}/\text{nitromethane}$  system the elemental analysis gives chlorine to metal ratio higher than 4. The empirical formula of the product is  $\{\text{CH}_{1.03}(\text{FeCl}_{4.30})_{0.034}\}_x$   $\Sigma$  % C,H,Fe,Cl = 100.95.

The Mössbauer spectrum of the sample doped to ca. 5.0 % reveals only the features characteristic of  $\text{FeCl}_4^-$ . The reduction of this sample to the maximum undoping level obtainable leads to the appearance of  $\text{Fe}^{2+}$  in addition to the already present  $\text{Fe}^{3+}$  lines (see Table 1).

TABLE 1 EPR and Mössbauer parameters of polyacetylene doped (oxidation part) and undoped (reduction part) in LiCl/FeCl<sub>3</sub>/nitromethane solution.

Doping with FeCl <sub>4</sub> <sup>-</sup>					
Dopant concentration from mass uptake (%)	FeCl <sub>4</sub> <sup>-</sup> EPR signal		(CH) <sub>x</sub> EPR signal	Mössbauer parameters at 4.2K	
	A/B	ΔH <sup>PP</sup> (G)	ΔH <sup>PP</sup> (G)	I.S. (mm/S)	Q.S. (mm/S)
0.00	invisible		0.85	not measured	
0.04	invisible		1.33		
0.20	1.0	431	1.31		
0.50	1.0	387	1.53		
0.90	1.3	530	1.57		
2.60	3.7	635	3.30	0.30	0.26
4.30	4.5	649	invisible		
Undoping					
2.60	1.2	467	3.41	not measured	
2.00	1.0	420	2.62	<u>Phase I ca. 70 %</u>	
				0.30	0.26
				<u>Phase II ca. 30 %</u>	
				1.08	2.70

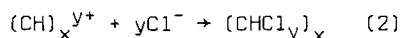
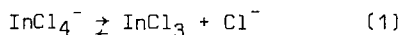
#### DISCUSSION AND CONCLUSIONS

The obtained results clearly show that doping-undoping cycles in LiCl/MCl<sub>3</sub>/nitromethane/(CH)<sub>x</sub> systems are not totally reversible. The dopant recovery at 5 % doping level is ca. 70-75 % after the

first doping-undoping cycle and still decreases after each additional cycle. For comparison, Kaneto *et al.* (4) reported significantly higher (86 %) charge recovery in  $\text{LiClO}_4/\text{propylene carbonate}/(\text{CH})_x$  system for comparable levels of doping. Such behaviour is indicative of irreversible side reactions occurring during the electrochemical doping and undoping in polyacetylene-metal halides systems. This conclusion is further corroborated by the EPR studies since the EPR line, becomes consistently broader when it returns to its symmetric shape after the oxidation-reduction cycle.

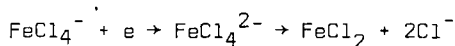
Since the elemental analysis for both  $\{\text{CH}(\text{InCl}_4)_y\}_x$  and  $\{\text{CH}(\text{FeCl}_4)_y\}_x$  systems show chlorine to metal ratio  $> 4$ , it seems probable that the doping-undoping cycle is accompanied by the chlorination reaction.

In the case of  $\text{InCl}_4^-$  the chlorination could be the result of a nucleophilic attack of the polycarbonium cation by  $\text{Cl}^-$  according to the following reactions :



$\text{InCl}_3$  can be easily removed from the polymer by washing the film. It is consistent with high current yields ( $> 100\%$ ) observed at the beginning of the undoping process.

In the case of  $\{\text{CH}(\text{FeCl}_4)_y\}_x$  another mechanism of chlorination is also possible. Since, as evidenced by Mössbauer spectroscopy, in electrochemically reduced samples  $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$  is present in addition to  $\text{FeCl}_4^-$  ions the following reaction can be postulated :



Mössbauer spectroscopy also shows that the majority of the residual dopant (ca. 70 %) retains its chemical form i.e.  $\text{FeCl}_4^-$  and only a smaller fraction is transformed into  $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ . The lack of success in the electrochemical removal of all  $\text{FeCl}_4^-$  suggests that the diffusion coefficient of  $\text{FeCl}_4^-$  significantly decreased



in the areas where some chlorination took place.

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