Electrical Conductivity of Polyaniline–Silver Nanocomposites

M. Varga, J. Prokeš

Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic.

P. Bober, J. Stejskal

Institute of Macromolecular Chemistry, Academy of Sciences, Prague, Czech Republic.

Abstract. We present a brief overview of the electrical properties of conductive composites containing silver and conducting polymer–polyaniline. Composites were produced by oxidation of aniline with silver nitrate in the presence of various acids playing the role of doping agents. A semiconducting behaviour was observed under the threshold about 21–27 vol.% of silver in composite and a metallic one above. From the temperature dependence of conductivity several charge transport mechanisms were proposed to explain experimental data with the most likely option of a superposition of the variable range hopping or the charging energy limited tunnelling model with the Arrhenius-like activated transport. An effect of dynamic vacuum on conductivity was discussed in terms of moisture removal and possible structural changes. The differences due to various dopants were found to be negligible.

Introduction

Electrically conducting composites containing noble metal and conducting polymer seems to be promising from the possible application point of view. As an example can serve catalytic use [*Della Pina et al.*, 2011] or the preparation of conducting inks [*de Barros et al.*, 2005]. Bulk silver shows the highest electrical conductivity among metals at room temperature and is an adept for producing conducting composites, either in organic or inorganic matrices. When metal is dispersed, the system can be classified as granular metal and shows changes in charge transport properties with the concentration of metallic particles in host matrix. For their high content a metallic behaviour with linear temperature dependence of resistivity is characteristic while for their low content a semiconducting behaviour is observed. A standard model for explanation of conductivity in such materials where small metallic particles were embedded in insulating matrix was developed [*Abeles et al.*, 1975]. It is referred as the charging energy limited tunnelling (CELT). Even though original ideas in the proposed model were later criticised, predicted soft-exponential temperature dependence is still valid. Nevertheless, since then a lot of theoretical effort was made on granular metals. Results are reviewed in, e.g., *Beloborodov et al.* [2007]. Also polyaniline belongs to the most prominent members of the family of conducting polymers. In order to explain a charge transport phenomenon in semiconducting state of conducting polymers, several mechanisms have been proposed [for a review see, e.g., *Kaiser*, 2001], mostly adopted from the field of inorganic amorphous semiconductors. Among the most discussed models belongs hopping family, represented by the famous variable range hopping (VRH) [*Mott and Davis*, 1977] giving the temperature dependence:

$$\sigma(T) = \sigma_0 exp\left(-\left(\frac{T_0}{T}\right)^{\gamma}\right) \tag{1}$$

with γ related to the dimensionality of system, σ_0 pre-exponential factor with often negligible temperature dependence, and T_0 describing details of the system, such as the density of states at the Fermi level, a nubmer of the nearest neighbour hopping sites, etc. Other models such as the correlated polaronic cluster tunnelling [*Zuppiroli et al.*, 1994], hopping in granular metals [*Sheng* *et al.*, 1973] and the Efros–Shklovskii hopping [*Efros and Shklovskii*, 1975] give the temperature dependence of conductivity in the form of the equation above with exponent 1/2. A slightly different behaviour one can obtain from the fluctuation-induced tunnelling (FIT) [*Sheng*, 1980]:

$$\sigma(T) = \sigma_0 exp\left(-\frac{T_0}{T+T_1}\right) \tag{2}$$

where σ_0 is conductivity of large conducting grains and T_1 has a meaning of limiting temperature. When $T << T_1$, temperature dependence of conductivity is fully determined by the pre-exponential factor. Obviously, all mentioned models lead to very similar and hardly distinguishable soft-exponential temperature dependence. Moreover, at higher temperatures an activated behaviour of Arrhenius type, formally the same as eq. (1) with γ equal to one, with activation energy E_A is commonly observed [*Pelster et al.*, 1994]:

$$\sigma(T) = \sigma_0 exp\left(-\frac{E_A}{k_B T}\right) \tag{3}$$

Since in our case we deal with both components able to carry the electric current, an interesting question appears, what would be the final conductivity, which component play a major role and how the overall transport is influenced by different factors, such as composition, dopant, etc. In composites where conducting particles are embedded in insulating matrix, conductivity is often dependent on the volume ratio of the conducting phase x and non-zero conductivity is observed when conducting pathways are form. This phenomenon is studied within so-called percolation theory which gives typically power law dependence:

$$\sigma(x) \sim (x - x_c)^t \tag{4}$$

where the critical value x_c is known as the percolation threshold and exponent t reflects the details of percolation model [*Kirkpatrik*, 1973].

An intesive study of polyaniline-silver composites prepared by oxidation of aniline with silver nitrate ($AgNO_3$) has been done in presence of different acids (acting as dopants) giving a high silver content composites ($\approx 69\,$wt.%) and various temperature dependence of conductivity [*Bober et al.*, 2011b; *Blinova et al.*, 2010]. Also combination with another oxidant ammonium peroxydisulfate (APS) resulting in variation of the silver content has been studied [*Bober et al.*, 2011a]. Both approaches became the starting point for our study but a deeper analysis of the electrical properties is of the main interest.

Experimental

Material

Composites, in a salt form, were prepared by oxidation of 0.2 M aniline with APS and/or $AgNO_3$ in different concentrations, 0–0.25 $\mathrm{mol\,L^{-1}}$ for APS, 0–0.5 $\mathrm{mol\,L^{-1}}$ for $AgNO_3$ in 1 M methanesulfonic (MSA) or acetic (AC) acid. Deprotonation, in order to obtain a base form, was achieved by immersion of samples in a large excess of 1 M ammonium hydroxide [*Bober et al.*, 2011a]. The material was prepared in a form of powder and then compressed by a manual hydraulic press into pellets.

Characterisation

The electrical conductivity at room temperature of highly conductive samples ($\sigma > 10^{-2}\ S/cm$) was measured by the four-point probe method in van der Pauw configuration (using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter and a Keithley 705 Scanner equipped with a Keithley 7052 Matrix Card). This technique was also used for temperature dependence study in the range 77–318 K (performed in a Janis Research

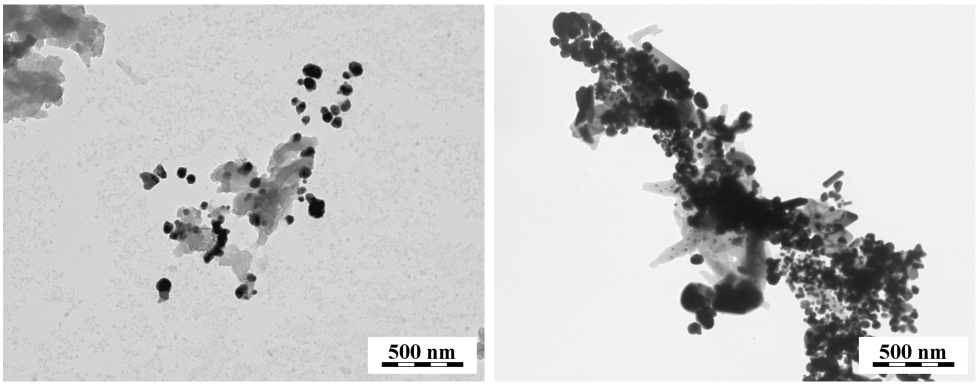

Figure 1. Example of polyaniline-silver composites morphology. Transmission electron micrographs of AC-salt with 5 vol.% of silver (left, a silver-poor system) and AC-salt with 25 vol.% (right, a silver-rich system).

VNF-100 cryostat using flowing stream of nitrogen vapor) with the samples were first treated several hours in dynamic vacuum (*ca* 10 Pa) at temperature 305 K to remove moisture. The method was used for a study of the time evolution of conductivity at elevated temperatures (*ca* 318 K) and dynamic vacuum $\approx 10^{-3}$ Pa as well. The conductivity of the resistive samples (bases, $\sigma \leq 10^{-2}$ S/cm) at room temperature was measured by the sandwich-like two probe method (using a Keithley 6517 Electrometer/High Resistance System) with gold electrodes evaporated on pellets. The density was obtained by the so-called Archimedes method (by using a Sartorius R160P balance), the weight silver content was determined from the residue after burning and both were used for the determination of silver volume fraction in composites. The morphology was studied by a transmission electron microscope (a JEOL JEM 2000FX).

Results and Discussion

Morphology

Polyaniline can be found in either nanofibrillar or granular morphology and serves as polymer matrix, *i.e.* is decorated by spherical silver particles and their aggregates (Fig. 1). A rather wide range of particle/cluster size was observed, starting from about 50 nm up to a micron. With increasing amount of silver nitrate in the reaction mixture number of silver particles also increased.

Conductivity vs. composition

Changing the proportion of silver nitrate in the reaction mixture a variability in silver content in the final product was achieved, within the range of 0–27 vol.% for salts respectively 0–30 vol.% in case of bases. A strong dependence of the electrical conductivity on metallic silver amount was observed (Fig. 2) with a critical value of its volume fraction (“threshold”) separating two qualitatively different regions. One being under the threshold with the conductivity about 10^{0} S/cm typical for PANI salts, showing no significant dependence on used dopant, resp. 10^{-6} S/cm for bases, a value 1000 times higher than is typical for silverless deprotonated PANI. This could be ascribed to the conductivity of a granular metal system embedded in an insulating matrix. The ohter region with typical conductivity about 10^{3} S/cm is above the threshold. The such high value of conductivity is believed to be a consequence of presence of conducting paths through the material due to high amount of silver. Since the insufficient number of experimental data did not allow us to determine the exponent and the threshold , see eq. (4), following from the percolation theory so far, we at least estimated the threshold being in the range 21–24 vol.% for salts and 25–27 vol.% for bases.

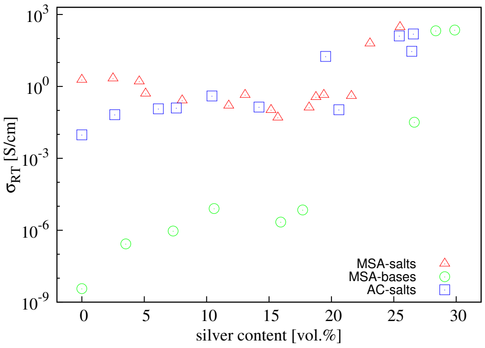

Figure 2. The dependence of the room temperature conductivity of polyniline-silver composites (salts of MSA, deprotonated bases of MSA, salts of AC) on the silver content.

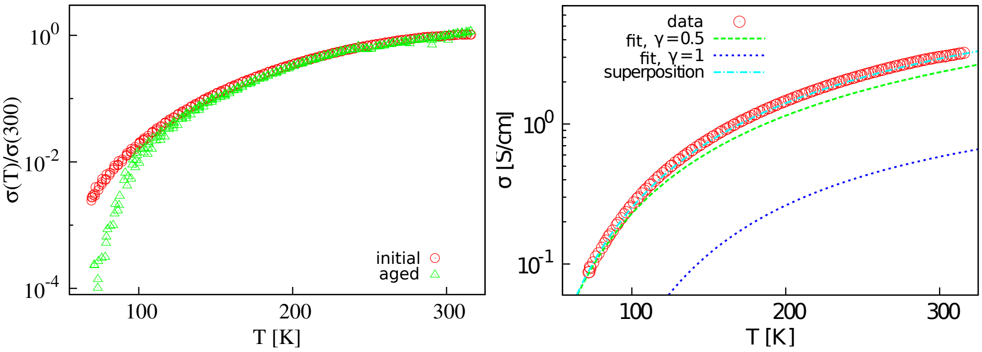

Figure 3. Semiconducting PANI-like behaviour of composites, 19 vol.% of silver (left). Experimental data (5 vol.%) fit by (1), (3) and (1)+(3) with exponent 0.5 (right).

Semiconducting region

As it has already been mentioned in the introduction, the temperature dependence of the conductivity can bring information about the charge transport mechanism in the system. First, a semiconducting behaviour was observed (Fig. 3) for salts with silver content under the threshold, again, very similar for both doping acids. Experimental data were fitted against the equations (1)–(3) but in the most of cases the best results were achieved by using superposition of eqn. (1) with exponent γ equal to 0.5 and (3) where both contributions are important in different temperature regions. The idea of two parallel mechanisms is supported by measurements on aged samples (Fig. 3 left), after about 18 months, where one (higher temperatures) remains more or less unchanged and the second one (lower temperatures) shows steeper decrease. While the superposition still satisfactory fit the data, any single mechanism does not without physically unrealistic set of parameters.

Even though the data were successfully fitted, the interpretation of obtained parameters is rather a tremendous task. Since the exponent 0.5 in eqn. (1) is probably the most frequent among theoretical models, it is impossible to satisfactory relate any microscopic description to experimental data only from the temperature dependence in the region 77–318 K. In our opinion, additional information from other experiments such as measurements of conductivity in variable magnetic field, electric field and cryogenic liquid helium temperatures can bring a deeper insight to the problem. Another option is to pay attention to the ageing of material since we believe to be unlikely that transport mechanism would change fundamentally with time. As the more probable scenario we expect changes in parameters that reflect changes in structure, for instance the size of metallic islands in the case of CELT.

The time evolution of the conductivity was studied first at elevated temperatures (305 or 318 K) and at ambient pressure, thereafter pump was turned on to see the effect of vacuum.

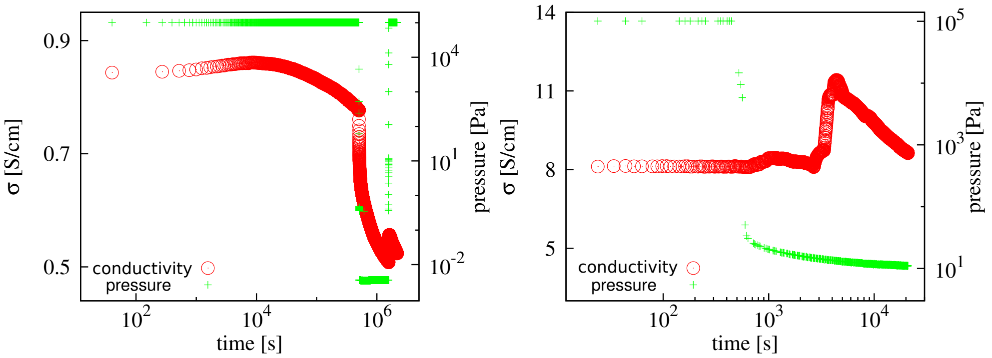

Figure 4. Time evolution of conductivity under different vacuum and temperature conditions. Ageing and moisture removal effects (left) and anomalous "peak" in conductivity (right).

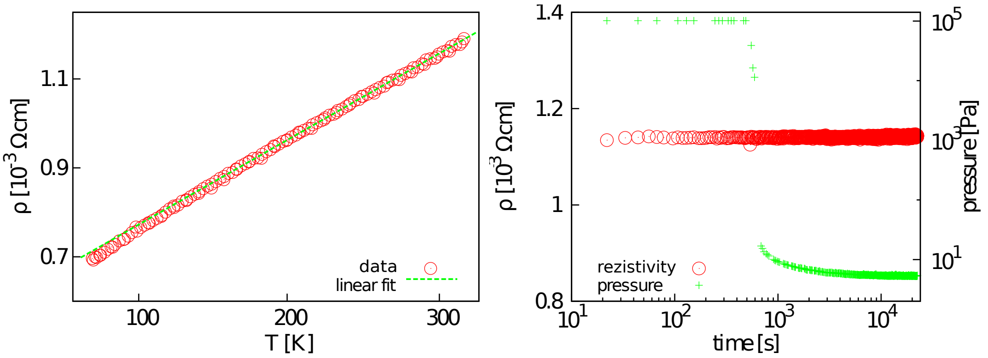

Figure 5. Metallic behaviour of composites above the threshold, 25 vol.% of silver, (left) and the independence of rezistivity on moisture (right).

We observed on one hand expected decrease (Fig. 4 left), first due to ageing/degradation at elevated temperatures [*Sixou et al.*, 1996] and moisture removal due to vacuum [*Pinto et al.*, 1996] where an exponential decrease was suggested [*Tang et al.*, 2008]. Since we believe that transport is mainly determined by polyaniline these results are not surprising. On the other hand there were anomalous changes in a form of "peaks" (Fig. 4 right) observed. The later is probably due to some internal structural changes but the proper origin is still questioned and the problem is open.

Metallic region

Above the threshold the composites acquire metallic character with conductivity as high as 10^3 S/cm and the linear temperature dependence of resistivity (Fig. 5 left). The values are two orders of magnitude lower than bulk silver shows. This is probably due to existence of finite number of conductive pathways via silver particles and enhanced electron scattering on the boundaries and interfaces as it was reported earlier [*Abeles et al.*, 1975]. The time evolution of conductivity confirms the key role of silver in transport since it is independent on moisture removal (Fig. 5 right).

Conclusion

Polyaniline–silver composites were prepared from two originally non-conducting components by oxidation of aniline with silver nitrate in presence of doping acids (MSA, AC). A second oxidant (APS) played a role in the control of the silver content in the final composite. Up to some value of the silver content (*ca* 21–24 vol.%) the electrical conductivity of the salts was not influenced by its presence and showed typical PANI-like semiconducting behaviour. In the case of bases, an insulating behaviour was observed with conductivity about 10^{-6} S/cm under the threshold of 25–27 vol%. Above the threshold the system turned to the metallic state with conductivity $\approx 10^3$ S/cm but still with values lower than bulk silver achieves. Several mechanisms were proposed for the description of the temperature behaviour of semiconducting samples typical for the class of conducting polymers or granular metals but further experiments (e.g., lower temperatures, electric and magnetic field dependence) are needed to distinguish among them. Time evolution of conductivity under vacuum and elevated temperature was also studied. Except the thermal ageing and the effect of moisture removal anomalous changes were observed, probably related to some structural changes.

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References

Abeles B., Sheng P., Coutts M.D., and Arie Y.: Structural and electrical properties of granular metal films, *Adv. Phys.*, 24, 407-460, 1975.

Beloborodov I.S., Lopatin A.V., Vinokur V.M., and Efetov K.B.: Granular electronic systems, *Rev. Mod. Phys.*, 79, 469-518, 2007.

Blinova N.V., Bober P., Hromádková J., Trchová M., Stejskal J., and Prokeš J.: Polyaniline-silver composites prepared by the oxidation of aniline with silver nitrate in acetic acid solutions, *Polym. Int.*, 59, 437-446,2010.

Bober P., Stejskal J., Trchová M., and Prokeš J.: Polyaniline-silver composites prepared by the oxidation of aniline with mixed oxidants, silver nitrate and ammonium peroxydisulfate: The control of silver content, *Polymer*, 52,5947-5952,2011a.

Bober P., Trchová M., Prokeš J., Varga M., and Stejskal J.: Polyaniline-silver composites prepared by the oxidation of aniline with silver nitrate in solutions of sulfonic acids, *Electrochimica Acta*, 56, 3580-3585,2011b.

de Barros R.A., Martins C.R., and de Azevedo W.M.: Writing with conducting polymer, *Synth. Met.*, 155, 35-38, 2005.

Della Pina C., Falletta E., and Rossi M.: Conductive materials by metal catalyzed polymerization, *Cat. Today*, 160, 11-27, 2011.

Efros A.L., and Shklovskii B.I.: Coulomb gap and low temperature conductivity of disordered systems, *J. Phys. C*, 8, 49-51, 1975.

Kaiser A.B.: Electronic transport properties of conducting polymers and carbon nanotubes, *Rep. Prog. Phys.*, 64, 1-49, 2001.

Kirkpatrik S.: Percolation and conduction, *Rev. Mod. Phys.*, 45, 574-588, 1973.

Mott N.F., Davis E.: in *Electronic Processes in Non-crystalline Materials*, p.35, Clarendon, Oxford, 1979.

Pelster R., Nimtz G., and Wessling B.: Fully protonated polyaniline: Hopping transport on a mesoscopic scale, *Phys. Rev. B*, 49, 12718-12723, 1994.

Pinto N.J., Shah P.D., Kahol P.K., and McCormickand B.J.: Conducting state of Pani films, *Phys. Rev. B*, 53, 10690-10694, 1996.

Sheng P.: Fluctuation-induced tunneling conduction in disordered materials, *Phys. Rev. B*, 21, 2180-2194, 1980.

Sheng P., Abeles B., and Arie Y.: Hopping conductivity in granular metals, *Phys. Rev. Lett.*, 31, 44-47, 1973.

Sixou B., Mermilliod N., Travers J.P.: Aging effects on the transport properties in conducitng polymer polypyrrole, *Phys. Rev. B*, 53, 4509-4521, 1996.

Tang S.J., Liu S.M., Chiu K.Ch., Wu Y.Y., Yeh, J.M.: Effects of dynamic vacuum-pumping and temperature dependence of dark electrical conductivity in polyaniline films made by various pressing pressures, *J. Phys. D: Appl. Phys.*, 41, 125401-125406, 2008.

Zuppiroli L., Bussac M.N., Paschen S., Chauvet O., and Forro L.: Hopping in disordered conducting polymers, *Phys. Rev. B*, 50, 5196-5203, 1994.