Composite solid electrolytes materials for the measurement of bioelectric signals. Paola Romagnoli^a, Maria Luisa Di Vona^a, Enrico Traversa^a, Livio Narici^b, Walter G Sannita^c and Silvia Licoccia^a

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Polymer based composite materials are extensively studied for a variety of biomedical applications.(1) We have previously reported (2) on the development of ionoconductor polymeric gels to be used in EEG extreme conditions recording in (emergency, experimental conditions "on the field", non-cooperative subjects etc.). The aimed application was the study the functions of the astronaut's brains during long space missions.(3) EEG recording concerns the measurement, amplification and registration of differences between fluctuating electrical field potentials as a function of time. By means of EEG registration a representation of the spatial distribution of the potentials over the scalp is obtained.(4) The electrical connection between the human subject and the analysing equipment is commonly established by an electrolyte bridge formed by liquid electrolyte or semi-fluid paste applied on electrode. The gel membranes that we have developed, were formed by a liquid electrolyte immobilized in a polymeric matrix; they achieved the mechanical characteristics suitable for the desired applications and produced samples with high conductivities values and producing EEG traces comparable to those recorded with conventional apparatus. The electrochemical properties of metal/gel and skin/electrolyte junctions cause, however, a steady electrical potential and an electrical impedance in the connection between tissue and apparatus. Both can restrict the performance of the recording system.(5) Furthermore, for the recording of signals in peculiar conditions it is important to use solid samples that would not spread on the skin and also that could be used without skin preparation. To overcome these drawbacks we have developed new water containing ionoconducting polymeric gel membranes. The preparation of the samples involved homogeneous dispersion of LiClO₄ in nonaqueous solvent, followed by addition of high molecular weight PMMA (polymethilmethacrilate) along with EtOH and H₂O. The solution was heated until complete gelatinisation occurred. Although their electrochemical response is good (the conductivity values are quite high, i.e. of the order of 10^{-3} S/cm at room temperature) these new system demonstrated to be unstable in time. We have then doped the membranes with different nanocrystalline ceramic oxide powders (Al₂O₃,TiO₂, SiO₂). It is in fact known that the use of ceramic fillers improves water retention characteristics, mechanical and electrochemical stability and elasticity of polymeric membranes.(6)

The new membranes have been electrochemically characterized by impedance spectroscopy and showed high and stable conductivity values for a long period of time (over two months). The intercepts with the real Z' axis in the spectra in Figure 1 show only a minor shift even after 60 days of storage and no deviation from linearity. Conductivity values were in the range $1.5 \ 10^{-3} - 3 \ 10^{-3}$. All the samples had the desired mechanical properties. Spontaneous EEG and visual evoked potential (VEP) recording have been made with our solid gels. All the polymeric electrolytes allowed the registration of electrophysiological cortical signals either spontaneous or stimulus-related, although the signals characteristics were not adequate in all cases. The performance of the Al_2O_3 doped membrane compared best with that of the standard wet Ag/AgCl electrode. It is worth noticing that all tests were performed without any special scalp preparation or liquid gel on subject with hair.

The different characteristics of the various ceramic fillers induce different interactions between the polymer chain and lithium salts and affect the electrical properties and the bioelectrical response of the composite system.



Fig.1: Impedance spectra of SS/ LiClO₄-gly-PMMA + TiO₂/ SS (SS stainless steel) cell at room temperature.

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