Sonic and Microwaves Assisted Redox Reactions of the Hydrolysates of Protein for the Preparation of Rechargeable Battery

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Summary: Long recharging time is one of the serious limitations of batteries. One of the best solutions for quick redox reactions *via* the use of microwave and sound-assisted reversible redox reaction is presented in this work. A wireless charged prototype battery based on the redox reactions of hydrolyzed waste protein was designed. The effect of experimental conditions like time of charging, nature of media and strength of the acid on the voltage of this prototype battery was investigated. The experimental data was explained on the basis of the previous work on protein peptides and amino acids by various workers.

Key Words: Wireless charging, Faster charging, Protein battery, Single cell battery

Introduction

Proteins and peptides are biomolecules of diverse function and chemical composition. All of these are the polymers of amino acids and associated with NH_2 and acid sites and have peptide linkage which may be a site of the reaction. Proteins, peptides and their monomers may pass through reversible redox reactions. These redox processes may either involve transfer of electron or proton, example of the proton transfer reactions includes cysteine-cystine transformations [1-4]. There are reports of the electron tunneling through proteins [5-8]. Redox reactions of the protein and peptides may have greater potential of the electricity generation and storage. It is the composition of proteins, peptides and amino acids that allows it to have both positive and negative charges under appropriate conditions. This charge gives it greater potential as charge carrier and charge storage molecules [9-11]. It is believed that these may also generate and store energy by absorbing energy for reversible redox reactions. This energy is stored as chemical energy and may reappear as electrical energy, if redox reactions are properly coupled. The generation of bio-electricity by the electric eel and shark are the best examples of bio-based *in vivo* electricity. The concept of protein battery was presented by our group [12]. This involves oxidative condensation or reductive de-polymerization which may also occur by radiations or sonic energy [13-16].

The present work is based on sono-chemical oxidation-reduction of hydrolysates of the proteins of fish scales which may be the peptides or amino acids obtained by the hydrolysis of fish scales. There are literature reports of the sono-chemical oxidation reduction. These redox reactions range from redox reaction of organic compounds to the formation of nanoparticles by sono-chemical process. There is literature reports about the sono-chemical synthesis of material used in batteries [17, 18]. Sono-chemical reactions are characterized for their speed and selectivity of products. These reactions may be utilized for the storage and transformation of energy into electrical energy. A number of methods are reported for charging of batteries other than contact process. These include charging by radio-waves, a seismic geophone, seismic piezoelectric accelerometers, photovoltaic cells, infrared p-v cells located inside the package driven by the heated package and sonic and ultrasonic energy coupled to the recharging circuitry *via* an acoustic transducer. None of these are based on any chemical reaction nor utilization of any waste material. The present work is based on the utilization of waste for the storage and transformation of energy [19-21].

The aims of present work are resource recovery from byproducts of fish industry which is protein, method for the generation of electricity and investigation of the material which transform other forms of energy into electrical energy. This work will be extended to investigate the effect of sonic waves and microwaves on the living things specifically the human beings to avoid the possible hazard. This work is based on the utilization of waste proteins for voltage generation through the use of sonic and

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microwaves energy where fish scales and broiler feathers were used as source of protein. Fish scales are mainly made of Type I collagen and feathers are made of keratins [22, 23]. The hydrolysis of fish scales solution may result in the formation of a large number of amino acids including methionine, cysteine and glutathione [24, 25]. However, keratin may result the formation of aspartic, glutamic acid, serine, threonine, glycine, alanine, valine, and lysine [26, 27]. The presences of oxidizable and reducible species in these solutions enable to prepare a battery by their coupling. This work will be extended to investigate the effect of sonic waves and microwaves on the living things specifically the human beings to avoid the possible hazard.

Experimental

Material and Method

In this study, fish scales and poultry feathers were used as sources of the protein. Both materials were obtained from retailers in the Shankar area of district Mardan Khyber Pakhtunkhwa, Pakistan through a random collection. The fish scales were composed of scales from the Raho and Chinese fish. These scales were properly cleaned from the blood using tape water and then distilled water. 20 g of clean and dry fish scales were transferred to a clean china dish followed by addition of 150 mL of 3% sodium hydroxide solution. It was heated to boiling on a hot plate with stirring followed by the addition of 100 mL of more sodium hydroxide. The dissolution was completed in 45 min, on cooling it was diluted to 250 mL and used as stock solution for cathodic half after filtration.

The anodic solution was prepared using feathers of broiler. Feathers were properly cleaned from the blood using tape water and then distilled water and were dried in the sun. 20 g of the feathers were initially heated in 150 mL of the 3% sodium hydroxide solution with stirring to facilitate dissolution. After 15 min heating it was followed by the addition of 100 mL more sodium hydroxide. Unlike fish scales this dissolution was completed in 30 min, on cooling it was diluted to 250 ml and used as anodic half of the battery after filtration.

Construction of the Battery

A single cell rechargeable protein battery was constructed using a single unit two compartment high density polyethylene container. Each of the compartments is characterized by its dimensions as 5x5x5 cm and act as two halves of cell. The two halves of cells were connected by a salt bridge made up of a cotton cloth wick of 3 mm thickness 3 cm width and 6 cm length. The graphite electrodes were mounted in a strip of a cardboard and were connected to each other in series through connecting copper wires. Some of the optimizations were carried out using a single cell battery and some by the use of multiple cells in series. The voltage was measured by the use of Fluke 115 multimeter.

Charging of the Battery

Protein battery was prepared by taking 50 mL of fish scales solutions in cathodic half-cell of battery followed by loading of 50 ml hen’s feathers solution in the anodic half-cell. The voltage of this cell was noted after placing the salt bridge and connecting the wires. The charging of battery was carried out in three separate sets of experiments; electrical, sonic, and microwave charging. Electrical charging of the battery was carried out using a custom made DC transformer having an out voltage of 24 volt and graphite electrodes. In case of sonic charging the solutions were directly placed in sonic bath. It was a sonic bath of power sonic 405 Hawshim Tech. Seoul Korea. The two solutions were sonicated for 5 min, however, this time was varied in time optimization experiment. On cooling for 5 min the two solutions were connected through salt bridge and the electrodes were placed in each of the solution followed by measurement of voltage by using the Fluke multimeter. Each of the experiments was conducted in triplicate and the average of the three reading was reported. In case of microwave charging each of the cathodic and anodic solution was exposed to 150 watt microwave power at 100 $^{\circ}$C and 120 psi for 5 min. This microwave assisted charging of the protein was carried out in CEM microwave synthesizer. Each of the solution was added to the corresponding half of the cell and connected through salt bridge. It was followed by placing the graphite electrode and measurement of voltage.

Results and Discussions

Theory of Wireless Charging and Protein Battery:

The concept of protein battery was presented by our group [12, 28] with the idea of oxidative condensation or reductive de-polymerization. The best example is the cysteine-cystine inter conversion in which bond formation and cleavage takes place is associated with consumption or generation of electrical energy. There are literature reports about the reactions of amino acids and proteins by the microwaves [29-31]. Herein, we initiated this for investigation whether this reaction occurs by the microwave irradiation or sonic energy. This can be extended to the effect of microwave radiations on proteins of living things. The possible damage and in some cases the curing may also be evaluated.

Investigation of the Optimum Time of Charging

The alkali hydrolysis of fish scales and feathers is actually the hydrolysis of Type I collagen and keratins, respectively [22, 23]. Fish scale hydrolysis forms a number of amino acids including methionine, cysteine and glutathione [24, 25]. However, keratin results in the formation of aspartic acid, glutamic acid, serine, threonine, glycine, alanine, valine and lysine [26, 27, 32, 33]. In both solutions oxidized and reduced forms of these amino acids specifically sulfur containing amino acids remain in equilibrium. Any change in equilibrium concentration may lead to the energy gradient and the flow of charge. This change in concentration may vary with variation in reaction time. Literature reports indicate that amino acids may pass through oxidation or reduction by the use of ultrasonic waves [16] the extent of these reactions is based on the dose and duration of the ultrasonic energies. Based on our previous work on protein battery this redox may be utilized for the preparation of a wireless charged battery using sonic or microwave energies. Literature reports indicate that the yield and nature of products of the sonic waves and microwaves-assisted reactions vary with variation in exposure time [24-36]. The life and even strength of the battery depends upon the number of active species [37, 38]. However, in case of amino acids excessive doses of the sonic or microwave energies may change the nature and behavior of these biologically important molecules which also change the voltage and behavior of the resulting battery. In this work, the time of charging was investigated as a function of voltage. The results of this study are presented in Table-1 and Fig. 1. It can be seen that in case of sonic and microwave charging the voltage of the battery remains the same throughout the investigated time. However, in case of the electrical charging continuous increase in voltage was observed up to 25 min. It may be due to the fact that the electrical charging results the formation of secondary products which may have greater differences in potential at oxidation and reduction halves. In case of the sonic and microwave charging, it is associated with a slight change in equilibrium constant of the redox mixture. It is clear from the difference in voltage of the battery before charging and after charging of the cell.

Table-1: Time optimization studies.

Time of charging	Charge before Charging	Electrical Charging	Sonic charging	Microwave Charging
5	100	1400	300	200
10	100	1400	300	200
15	100	1500	300	200
20	100	1500	300	200
25	100	1700	300	200
30	100	1700	300	200

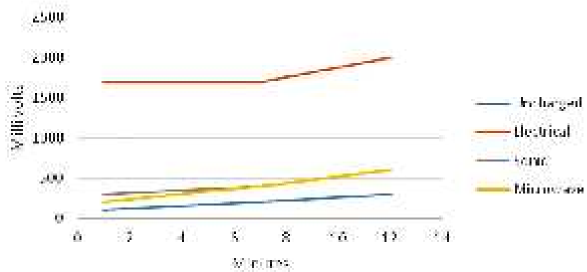

Fig. 1: Optimization of Charge duration using various sources of charging.

The Effect of Media on Charging of the Cell

The nature of electrolyte is one of the important parameters which always affect the strength and power of the cell [39, 40]. This may also depend upon the pH or acidity and basicity of the media. The effect of acid, base and neutral systems is believed as having more profound effect on the redox reaction of the amino acids, peptides and proteins [41-43]. It may also play role in hydrolytic degradation and condensation of the proteinaceous entities [44, 45]. In this study, the effect of media on the voltage of battery was investigated using acidic (pH 1), basic (pH 12) and neutral (pH 7) solution of each of the fish scales and feathers separately. The results of this study are presented in Table-2 and Fig-2. Each of the single cell battery was treated with the corresponding source of energy for 25 min. It can be observed from that media of the reaction has significant effect on the voltage of battery. It is due to feasibility of the formation of large quantity of the electro-active species in the acidic media, the resulting cell has greater voltage both in untreated and all the treated forms. Further in case of each of the neutral and acidic media the voltage of sonic and microwave charging is the same with a difference of 100 millivolt in case of the neutral solutions. The trend of basic and neutral solution is the same in case of electrical charging. It might be due to the high pH where the NH_2 group is inactive due to basic media and might be acidic sites are too week to act as active acid. Therefore, the voltage pattern for electrical charging remains the same in case of basic and neutral media.

Table-2: Effect of Media on Electrical Charging.

Media	Voltage before Charging	Electrical Charging	Sonic Charging	Microwave Charging
Basic	100	1700	300	200
Acidic	300	2000	600	600
Neutral	200	1700	400	400

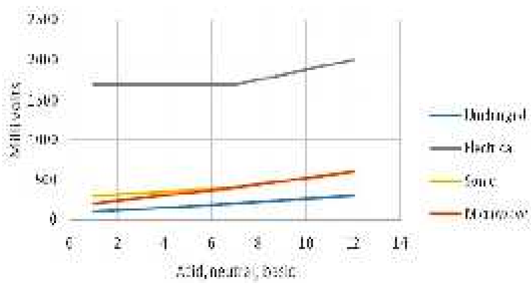

Fig. 2: Optimization of media using various sources of charging.

Effect of the Strength of Acid on Charging

Both the wireless and electrical charged protein batteries are based on the redox reactions and electrochemical transformation of the amino acids, peptides and protein moieties. Acid solutions for these cells may have two roles; electrolyte and reactant or catalyst for redox reactions. Optimum concentration of the acid may help in obtaining stable and power full batteries and efficient storage of energies in the form of electrical energy. Many of the electrochemical reactions depend upon the strength of acids [46-48]. Inspired from those and high voltage of the acidic media in our investigations, we have investigated the effect of strength of acid on voltages of the cell. These investigations were carried out using HCl in the range of 0.1-1 M. Each of the single cell battery was charged for 25 min. Results of these investigations are presented in Table-3 and Fig-3. It can be observed that the strength of acid in the investigated region have no effect on the voltage of uncharged cell. This indicates that the value of equilibrium constant remains the same when no energy is applied. This trend is different in case of the electrically charged, sonic and microwave charged cells. In case of electrical charging the voltage was constant up to 0.4 M of the acid. A decrease in voltage is observed at molarities of acid solution greater than this. This might be due to the formation of polymeric species at this high concentration of acid by the use of electrical energy. These may have either lower redox activity or slower mobility due to bulky nature. A regular pattern can be observed in case of sonic and microwave charging. Its optimum concentration may be 0.4 M. In case of the acidic media. It was observed that the voltage of protein battery is greater in acidic solution as compared to neutral and basic solutions both in electrical and wireless charging.

Table-3: Effect of acid strength on charging.

Concentration of acid (M)	Voltage before Charging	Electrical Charging	Sonic Charging	Microwave Charging
0.1	400	2000	500	500
0.2	400	1900	500	500
0.4	400	2000	600	600
0.6	400	1800	400	600
0.8	400	1500	400	400
1.0	400	1000	400	300

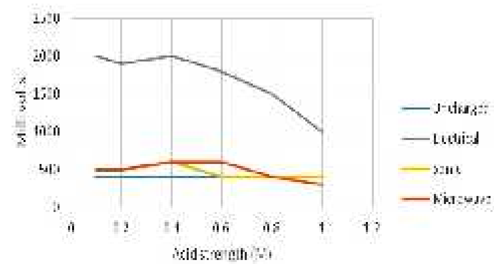

Fig. 3: Optimization of acid strength using various sources of charging.

Effect of the Nature of Acid on Charging

In addition to its function as electrolyte acids may also act as reactant [49]. The reactions of amino acids, peptides and proteins may involve the formation of peptide or degradation of the peptide linkage which is catalyzed by acids or bases [50-53]. In case of electrochemical reactions acids may also act as carrier of the charge in addition to facilitation of the reactions [54]. The effect of acid on electrochemical, sonic and microwaves assisted charging of the battery was investigated using four acids in 0.1 M concentration; all were monobasic in nature except phosphoric acid. Each of the experiments was conducted using the optimized time interval of charging. Results of this study are presented in Table-4. It can be seen from the results that variation in nature of the acids plays a vital role in the voltage of this one cell battery. In case of HCl the voltage was highest. This is due the fact that HCl helps in facilitating the electrochemical redox reaction of both the keratin and collagen. In case of acetic acid the results have quite contrast for all types of charging procedures. The voltage has been increased for sonic charging and decreased for both electrical and microwave assisted charging. It may be due to condensation of acetic acid with amino acids or peptides to form products less vulnerable to redox reactions. In case of boric acid the voltage of uncharged battery is 50% less than hydrochloric acid and acetic acid. It may be due to the reaction of amino acids with the electron deficient boron acid.

The microwave and sonic charged cells also show less voltage.

Table-4: Effect of the nature of acid on charging and voltage of cell.

Acid	Voltage before Charging	Electrical Charging	Sonic Charging	Microwave Charging
Hydrochloric acid	400	2000	600	600
Acetic acid	400	1700	750	300
Boric acid	200	1900	500	300

Conclusion

Sonic and microwaves-assisted reversible redox reactions were successfully used for charging of a single cell battery. The strength and power of this battery may be improved by proper selection of the experimental conditions and coupling of more than one cell. This is a faster charging battery and may be employed for powering of household appliances. This work can be extended to the *in vivo* effects of sonic and microwaves on the protein.

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