

## Electrochemical Studies of Some Organic Conducting/Super Conducting Materials

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### Introduction

The properties of C<sub>60</sub>-fullerene have been widely investigated. For example, doped fullerenes such as K<sub>3</sub>C<sub>60</sub>, Rb<sub>3</sub>C<sub>60</sub>, K<sub>2</sub>RbC<sub>60</sub>, which exhibit superconductivity or ferromagnetism, underscore the importance in applications such as superconductors, photo-electrochemical devices and sensors [1-2]. Electrochemical studies, which are inherent in this study also have received much attention in recent years [3-8]. Earlier voltammetric studies of a solid "film" obtained by adhering an array of microcrystalline C<sub>60</sub> on the solid state electrode surface describe how the reversibility of C<sub>60</sub> redox reaction of the "film" is dependent on the size of cation in appropriate electrolytes usually nonaqueous solvent and to what extent the film is reduced. The study on the incorporation process of cation such as tetrabutylammonium ion, NBu<sub>4</sub><sup>+</sup> into the C<sub>60</sub> microcrystals' lattices under cyclic voltammetric time scale has detected evidence of nucleation and growth processes in previous studies [5-6]. Although solid phase voltammetry of C<sub>60</sub> in nonaqueous media is widely reported, it is less so in aqueous media [5-6]. In this work, we attempt to determine the electrochemical properties of the fullerene "films" in aqueous media including its reactivity, stability and effect of doping including mixed doping of fullerene "films" and their conductive behaviours as possible electrode materials. The fullerenes of interests include M<sub>n</sub>C<sub>60</sub> (M= Li<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>, Rb<sup>+</sup>, n = 1-6) and their dopants.

### Materials and Methods

C<sub>60</sub> (Fluka, 98%, HPLC), alkali metal salts of perchlorate and chloride were used as received. Two methods were used to transfer solid C<sub>60</sub> onto working electrode surface. The first one was mechanical attachment technique

(MA). This method includes direct use of solid C<sub>60</sub> in powder form. The second method was known as solvent casting (SC) method. It was done by evaporating certain volume (in μL) of 0.15mM C<sub>60</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) onto the fresh working electrode surface. The working electrode surface with well-coated C<sub>60</sub> microcrystals layers would then be tested with various voltammetric technique modes of the electrochemical workstations (Model BAS 50W or 100W) such as cyclic voltammetry, chronocoulometry and bulk electrolysis (BE). A conventional three-electrodes configuration was employed, platinum wire as the counter electrode, silver-silver chloride (Ag/AgCl(3M NaCl)) as the reference electrode. Working electrode used was 3 mm diameter Glassy Carbon disk. The scanning electron microscope (Model JEOL JSM-6400) was used to study the surface morphology of C<sub>60</sub> before and after electrolysis. The fulleride salt was generated by holding the potential of the basal plane pyrolytic graphite electrode at -1.800V vs Ag/AgCl for 1 minute in an appropriate electrolyte using the BE mode. *In situ* electrochemical optical microscopic studies of C<sub>60</sub> in aqueous electrolyte were performed using a modulated Inverted optical microscope coupled to BAS 50W. An electrochemical quartz crystal microbalance (Model EQCM 500, coupled to BAS 50W) was used to assess any change in its mass under cyclic voltammetric conditions.

### Results and Discussion

Extensive voltammetric studies have been undertaken on microcrystalline C<sub>60</sub> fullerene particles adhered to a solid electrode surface and placed in contact with alkaline ion containing electrolyte. Comparison of adherence techniques such as solvent casting and mechanical transfer methods are made to assess if the type of adhered techniques has any

significant influence on the observed electrochemistry. Solvent casting method was found to produce three peaks potential for C<sub>60</sub><sup>0/n-</sup> redox couple as compared to a single and large peak produced when mechanical transfer technique was employed. When the reduction potential of microcrystalline C<sub>60</sub> in the presence of K<sup>+</sup> is compared with other cations such as Li, Na, Rh and Cs, it is observed that the shift of reduction potential follows the change in the hydration energy in the order of Cs>Rh>K>Na>Li. In mixed electrolytes study of CsCl and KCl, the reduction potential and peak shape of C<sub>60</sub><sup>0/n-</sup> redox couple during cyclic voltammetry was observed to change with concentration of the cations and the observed electrochemistry could be attributed to a cation exchange mechanism. The reduction of C<sub>60</sub> was irreversible, as the reoxidation process did not produce any observed electroactivity. The investigation of the reduction of solid C<sub>60</sub> in aqueous solution containing 0.1M K<sup>+</sup> under *in-situ* electrochemical optical microscope (20X magnification) and quartz crystal microbalance reveal that there is no evidence of compound dissolution nor a decrease in mass as the C<sub>60</sub> compounds is still attached on the electrode surface after continuous potential cycling. Thus, it is clear that the loss of faradaic current of K<sub>n</sub>C<sub>60</sub> on the reversal sweep is not due to the dissolution, but rather the formation of a passive coating of an/some irreversible or non-electroactive salt/s. It is known that the secondary reduction processes may form a real protective layer on the outer surface of the film, preventing its complete degradation and thus allowing its further use in electrocatalysis. The reduction of C<sub>60</sub> in the presence of K<sup>+</sup> which was irreversible has the following equation: C<sub>60</sub> + nK<sup>+</sup> + ne<sup>-</sup> = K<sub>n</sub>C<sub>60</sub>. Based on the area / charge under the cv curves, the number of electron trans-

ferred per molecule was determined to be close to 3. Hence, the formation  $K_3C_{60}$  fulleride was expected to pre-dominant as it is also structurally more favourable as it requires only a slight rearrangement and expansion of the  $C_{60}$  crystals structure as compare with those of other  $K_nC_{60}$  (1 or 6) species which was expected to be presence in a small amount. In the presence of increasing amount of KCl electrolyte ranging from 0.05M to 2.0M, the reduction peak of  $C_{60}$  shifts in a positive direction indicating presence of a favourable reductive over potential. Since ion pairing, asymmetry and electrophoretic effects are easily felt at a higher concentration of electrolyte, a moderate range of 0.1 to 1M supporting electrolyte are sufficient in most of the voltammetric experiments. When  $Cs^+$  was added to KCl in increasing amount in the order of 2:8, 5:5, 8:2 ( $CsCl$ :  $KCl$ ), the number of reduction peaks gradually diminishes from three to one and the peak potentials for the overall waveforms shifted in a more negative direction. The cyclic voltammogram assumes the character of  $Cs_nC_{60}$  fulleride when the  $Cs$  dopant was increased. Mixed fullerides, predominantly  $K_{3-x}Cs_xC_{60}$  ( $x=1-2$ ) was probably obtained via ion exchange reaction between the  $K^+$  in the reduced fulleride with the  $Cs^+$  added. Similar trend of result was reported for the other mixed electrolytes including  $K_{3-x}Rb_xC_{60}$ ,  $K_{3-x}Li_xC_{60}$ ,  $Rb_{3-x}Cs_xC_{60}$ . From the scan rate study of  $C_{60}$ , a linear scan rate dependence at moderate scan rate and a sharp increase in current and the charge transferred with increasing scan rate of up to 200 mV/s was obtained. At higher scan rate, the currents and the calculated charge transferred increase more slowly, indicating that the surface species were involved in the reactions (surface-confined process). A double step chronocoulometric experiments was carried out for  $C_{60}$  attached to a GC electrode via solvent casting and in contact with 1M KCl aqueous electrolytes. The Anson plot shows that during the reduction of  $C_{60}$ , there was an initially rapid increase in charge with time, corresponding to the reduction of the majority of the surface confined  $C_{60}$  microcrystals; however during the reoxidation step there was an absence of electroactivity as was evident from its charge vs sq. root of time line coinciding with those of the background line. The observation has con-

firmed the presence of a surface-based irreversible redox process of  $C_{60}$  in the presence of  $K^+$  containing aqueous electrolyte. Surface structure of solid  $C_{60}$  coated onto basal plane graphite electrode before and after electrolysis in water containing variety of alkali-metal salts was irregular, consisting of crystallites of random sizes. Reduction of  $C_{60}$  microcrystals in  $K^+$  containing aqueous electrolyte, formed typical and shapely microcrystals of  $K_nC_{60}$ , fulleride with sizes ranging from 1-5  $\mu m$  slightly larger in size as compared to those obtained before electrolysis with size ranging from submicron- ca.3  $\mu m$  indicating the presence of a surface process of solid - solid transformation.

### Conclusions

A large reductive waveform of the first negative scan of an array of microcrystals of  $C_{60}$  attached at the glassy carbon electrode was observed over the potential range of -1.3 - -1.8V with no reoxidation wave on the reverse scan in aqueous electrolyte containing alkaline ion. These data indicate the presence of (chemically) irreversible electrochemical intercalation of  $C_{60}$  with the formation of mixed fulleride of  $K_nC_{60}$  ( $n=1-6$ ).  $K_3C_{60}$  species probably predominated over other type of fullerides. Similar observation was also observed for fulleride with unidentical dopant such as  $K_{3-x}Rh_xC_{60}$ . Electroactivity of  $C_{60}^{0/n-}$  was lost on subsequent scans indicating that the complete reduction of  $C_{60}$  occurred. Evidence favoring the irreversible intercalation of cationic dopant in the lattices of  $C_{60}^{0/n-}$  rather than the dissolution process was obtained from both studies using *in-situ* electrochemical optical microscope (20X magnification) and quartz crystal microbalance. The pattern of a cyclic voltammetric (cv) waveform for  $C_{60}$  reduced in  $K^+$  containing aqueous electrolyte was affected by the method of transferring  $C_{60}$  (MA or SC) and the type and concentration of cation but independent of the type of anion presence in the supporting electrolyte under similar voltammetric conditions. Linear dependent of scan rate on peak height and the chronocoulometric data and the slightly larger crystal size observed after reduction of  $C_{60}$  indicates the presence of a surface process involving solid - solid transformation.

### Benefits from the study

The study has enabled us to gain further insight into the solid state reactions taken place at the microcrystal-electrode-electrolyte interfaces of  $C_{60}$  fullerene, helped in the preparation of 3-dimensional superconducting materials of low density of  $K_3C_6$ ,  $K_{3-x}Rh_xC_{60}$  and related dopant using electrochemical intercalation instead of using the more complicated and expensive method such as vapour phase intercalation. The study also suggests the use of  $C_{60}$  fullerene as mediator or electrocatalyst for mediating the more difficult and irreversible electrode processes of some important compounds. Preliminary work in the laboratory has demonstrated that the  $C_{60}$  coated electrode has potential as a mediator for the electro-oxidation of vitamin E and cysteine.

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