Plasmonic Optical Fibre Sensors for Electrochemical Activities Monitoring in Energy Storage Devices

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Abstract. Surface Plasmon resonance (SPR) optical fibre sensors can be used as a cost-effective and relatively simple-to-implement configurations for in situ high sensitivity electrochemical measurements. The flexible configuration, miniaturized size and remote operation ability offer them a multitude of opportunities for single-point sensing in hard-to-reach spaces. The nano-scale plasmonic metal-coating over optical fibre offers the sensor the ability to monitor the electronic and optical information simultaneously, with unprecedented sensitivities and limits of detection. Meanwhile, such sensor provides a multi-resonant mechanism of optical modes (cladding modes and core mode) for high accuracy plasmonic interrogation and inherent elimination of environmental cross talk. In this paper, we briefly introduce the principle and implementation of electrochemical plasmonic optical fibre sensors based on a tilted fibre Bragg grating imprinted in a commercial single-mode fibre and coated with a nanoscale gold film, and our recent studies of in situ and continuous monitoring the electrochemical activities (the potential and the stored charge) of supercapacitors for energy storage devices.

1. Introduction

Renewable energy produced from sun, ocean and wind can be transferred into electricity, which has been demonstrated a feasible way to relieve the energy crisis highly dependent on fossil fuels. However, the key problem is that renewable energy cannot be steadily and continuously obtained. Therefore, the technology and devices for renewable energy storage are very important [1]. As one of the most appealing energy storage devices, supercapacitors can be used as alternative of batteries owing to their high energy density, long cycle life and essential safety.

In order to better understanding the operation mechanisms and increase the charge efficiency of supercapacitors, continuously monitoring the detail working status of supercapacitors is necessary. Electrochemical surface plasmon resonance offers a promising way to simultaneously explore optical and electrochemical properties of chemical matrix accompanying redox reactions [2,3]. The increased sensitivity achieved with plasmon waves arises because of the large localization of electromagnetic energy in the layer immediately adjacent to the metal surface [4]. Any perturbation in that layer, such as the bonding of analytes on receptor molecules modifies the local refractive index of the dielectric and the plasmon phase velocity. Recent studies like the plasmonic imaging of surface charge density,

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single nanoparticle electrochemistry, plasmonic monitoring of charge status of small molecule. All above experiments are carried out using a bulky prism, it may be hard to be employed in hard-to-reach space or long distance environment monitoring.

Herein, we report the first application of in situ monitoring electrochemical activity of supercapacitors using plasmonic optical fibre sensors and demonstrate the intrinsic relationship between the charge state of supercapacitors and variation of optical surface plasmon resonance (SPR) [5]. The optical fibre sensor proposed here consists of a gold-coated tilted fibre Bragg grating (TFBG) imprinted in a commercial single mode fibre core, in which the nanometric-scale gold coating over the fibre surface offers the simultaneous detection of both the electrochemical information (electrochemical current) and the optical information (surface plasmon wave). Such plasmonic optical fibre sensor is cost-effective and relatively simple-to-implément alternative to well established bulky prism configurations for high sensitivity biochemical and electrochemical measurements. Its tiny size makes it feasible to be inserted into various hard-to-reach environments for in situ detection either as a hand-held probe or as a set of remotely operated devices along a fibre-optic cable, especially for environmental monitoring over the urban and suburban areas. The proposed in-fibre plasmonic biosensor shows a real time electrochemical and photochemical response to charge-discharge states of the supercapacitors and a minimal cross-sensitivity to temperature (through referencing of the spectrum by the core mode resonance). The sensor fabrication (UV-light grating-inscription and surface nanometric-coating) does not impact the structural integrity of the fibre so as to ensure the sensing stability and reproducibility. Finally, our study on the reproducible relationship between the optical response of SPR and the charge state of the supercapacitors in situ will be helpful to the understanding and evaluation of the operation quality of supercapacitors in active service.

2. Principle and Experiments

The electrochemical plasmonic fibre-optic sensing system is shown in Fig. 1, which in orderly comprises a broadband light source with bandwidth from 1250 to 1650 nm, a polarizer, a polarization controller, a circulator, a tiny plasmonic optical fibre sensing probe and finally an optical spectrum analyzer. Meanwhile, an electrochemical workstation is used for performing electrochemical measurement and collecting data related to supercapacitor. The computer was used to collect data of optical spectra and electrochemical curve spectrum simultaneously. The entire plasmonic fibre-optic sensing probe is very compact, with a size of 30 mm in length and 0.125 mm in diameter (as the yellow part shown in Fig. 1), and the fibre sensor was tightly attached on the surface of the supercapacitor electrode.

Fig.1. Experimental setup of plasmonic fibre-optic sensing system for monitoring charge state of supercapacitor.
CV curves measured at three different scan rates, i.e. 10 mV s\(^{-1}\), 15 mV s\(^{-1}\) and 20 mV s\(^{-1}\) were collected and shown in Fig. 2(a). The SPR spectra of the developed sensor corresponding to the three voltammetry tests at different scanning rate were recorded. The variations of SPR intensity during the charging and discharging process were calculated and are presented in Fig. 2(b). Figure 3(a) shows the current intensity response of supercapacitor for 5 cycles charging and discharging of the supercapacitor at two potential points (0 V and 0.8 V), which is obtained by electrochemical workstation. At the same time, the optical spectral responses of the SPR amplitudes were recorded, as shown in Fig. 3(b). Over the repeat tests, the plasmonic spectral responses for different charge-discharge states of the supercapacitor have been achieved in real time and there was a close and reproducible relationship between the intensity change of the optical SPR and the charge state of the supercapacitor. Meanwhile, over all the charging process, the core mode does not change during the whole detection process (see the red curve shown in Fig. 3(b), which is completely unaffected by the electrochemical activities over fibre surface. This unchanged core mode demonstrates that the sensing system is stable (no power fluctuations for the light source and transmission lines) and the temperature of surrounding environment keep unchanged. Therefore, the intensity variations of SPR resonances are only caused by the electrochemical reactions over fibre surface (cause by the supercapacitor charging). This is very important to ensure the reliability and stability of the sensor.
Figure 4 shows the relationship between the maximum stored charge ($C_{\text{max}}$) and the corresponding SPR intensity variation ($\Delta\text{SPR}$) for three repetitions of the measurements at each scan rate. A linear fit of the data indicates a relationship between $C_{\text{max}}$ (in mC) and $\Delta\text{SPR}$ (in dB) expressed as $\Delta\text{SPR}=-0.036 \times C_{\text{max}}-2.07 \times 10^{-5}$, with a regression coefficient $R^2$ of 100% and repeatability of 97.5% (1-$\Delta\text{SPR}_{\text{error}}/\Delta\text{SPR}_{\text{average}}$).

3. Conclusions

The feasibility of plasmonic optical fibre for in situ electrochemical measurement of energy storage devices (here supercapacitors) has been experimentally demonstrated. Such sensor not only provides optical SPR information for real time supercapacitor monitoring, it also offers an optical core mode which is inherently able to eliminate the potential environmental cross-talk. The flexible shape, compact size and remote operation ability make such plasmonic optical fibre sensors a multitude of opportunities for electrochemical monitoring in various hard-to-reach spaces while it operates, and over its lifetime.

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