Ballistic Kevlar fabric with energy storage properties

Y. Chao[1], T. Bussell[2], C. Wang[1], **J. Ding[2]**,

[1] *ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, AIIM Facility, University of Wollongong, NSW, Australia*
[2]*Land Division, Defence Science & Technology Department of Defence Melbourne, VIC, Australia (Jie.Ding@dst.defence.gov.au)*

Abstract. Shear thickening fluids (STF) are a promising component of advanced body armour materials for improved protection and flexibility. They can improve ballistic fabrics resistance to penetration by bullets, fragments or a knife without compromising weight, comfort and flexibility. Flexible body armour that allows for the wearers' maximum freedom of movement is highly desirable, especially for elbow and knee joints. Currently, batteries and power systems are required to be carried in large quantities by individual combatants due to the demands of modern warfare technology. This is a key challenge in the design of modern integrated soldier combat ensembles (SCE). It calls for the components of a SCE designed with multifunctionality. We have demonstrated success in turning STF body armour into a battery system which provides not only power but also protection against bullet impacts. Such multifunctional energy storage systems can share space and weight with existing body armour. Here, we report novel multifunctional ballistic Kevlar fabric for elbow and knee guards with energy storage properties. Lithium batteries composed of Kevlar electrodes and STF electrolyte has been developed; their electrochemical performances and protection properties against a range of kinetic impacts have been evaluated. Such batteries are capable of efficiently and safely storing power energy. It can also offer equivalent ballistic protection levels to common soft armour. The effect of shearing and bending (flexion moment and rotation) of knee and elbow joints on rheological properties of STF and electrochemical performance have been investigated.

I. INTRODUCTION

Throughout history, personal armour systems have been practical only when they have been able to provide adequate protection against prevailing threats whilst not impairing the wearer's ability to perform the tasks. Today's infantry soldier often packs more than 60 kgs and still has incomplete ballistic/blast protection. One area of increasing physical burden is in batteries to store electrical energy. Power systems carried by an individual combatant are becoming more demanding in terms of quantity and it is now a critical risk in the design of modern integrated soldier combat ensembles (SCE). It is therefore an advantage if components of a SCE are designed to perform more than one function. The development of shear thickening fluids (STF) battery offers potential to reduce the total number of systems carried by an individual combatant by combining the protective nature of body armour components and the storage of electrical energy. Extensive research is being undertaken within our group in this area [1–3]. Here we report a battery whose configuration is identical to "liquid body armour". Two basic components of "liquid body armour" were used to assemble the battery.

Adding STF into ballistic fabrics to generate "liquid body armour" has sparked significant attention, as it can improve the kinetic resistance of fabrics with more flexibility. A significant amount of research has been conducted on liquid body armour at the same areal density as conventional ballistic and stab resistant solution [4–10]. Current body armour systems are designed and implemented with a combination of different types of materials, such as ceramic, metals, polymers, ballistic fabrics and composite materials, achieving ballistic/blast protection through material layers with specific functions. The key issue is that if we provide the same level of protection to the extremities, such as arms, legs or neck as the torso, current body armour materials are far too stiff and bulky to allow wearers to move freely. Most modern body armour comprises many layers of woven Kevlar, sometimes with ceramic plates to give extra protection. For example, up to 30 or 40 layers of Kevlar are needed to offer sufficient protection; however, large number of layers of Kevlar would be too stiff and bulky for use as sleeves, trousers, and so on. Novel liquid body armour based on STFs has shown promising prospects towards improved protection and flexibility.

Shear thickening has long been a topic of interest. It is an example of a non-Newtonian fluid, often termed a dilatant fluid. At low shear rates, the fluid has low viscosity, acts as a lubricant and flows

https://doi.org/10.52202/078352-0011

easily. However, when an impact is applied (resulting in higher shear rates), the fluid adopts a solid-like state and due to a rapid increase in viscosity becomes less penetrable. More recently, the property has seen use in developing smart materials and composites [2,11–17] as their unique material properties make them ideal for many applications [2,18,19], including liquid body armour [4]. Various mechanisms have been proposed for the operation of STFs, including the formation of particle clusters by hydrodynamic lubrication forces [2,11], granular dilation [11], or impact activated solidification [13]. Simulations and experimentation have since shown that reversible shear thickening results from the formation of hydroclusters, temporary stress bearing aggregates of particles that form as a result of short range hydrodynamic lubrication forces overcoming the repulsive forces between particles during shear, as shown in Figure.1. Chains of these hydroclusters form as their numbers grow as a result of increased shear rate, resulting in larger aggregates forming which can jam flow [20]. An underlying order-disorder transition is not a requirement, but can occur in some systems prior to hydrocluster formation.

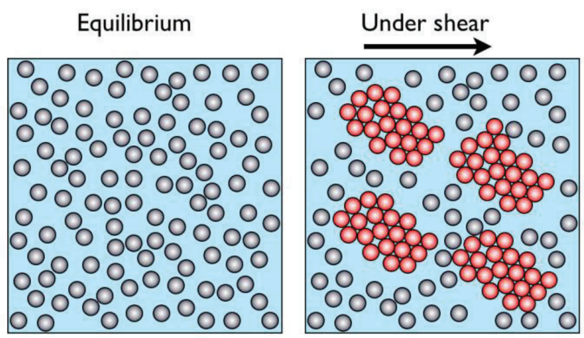

Fig.1 Schematic of particles forming hydroclusters under shear.

The ultimate goal is to create a ballistic battery that can not only share the space but also the weight of existing body armour, in order to improve the safety of batteries as well as lessen the burdens of the military personnel. This paper presents the results of work to develop materials that offer the potential of safe storage of energy, combined with an element of protection against kinetic threats. The novel lithium ion batteries were fabricated with a combination of Kevlar electrodes and STF electrolyte. To employ non-conductive Kevlar fabric as electrode substrates, silver plating process was used as a solution. After growing silver on the surface of Kevlar, high conductivity was obtained throughout the fabric. This work also investigated the effect of silver coating amount on the conductivity of Kevlar fabric, and the electrochemical performance of batteries using graphite on silver-coated Kevlar fabric (Ag-Kevlar-G). The soft-amour type of battery composed of Ag-Kevlar electrodes and STF electrolyte was also investigated.

2. EXPERIMENTAL

2.1 Preparation of silver-coated Kevlar and characterization

The Kevlar fabric was purchased from Colan Australian. Silver layer was chemically plated on the Kevlar fabric through a modified silver plating method (**Figure 1**) [20–22]. Briefly, Kevlar fabric was cut into designated sizes, e.g., small round pieces with a diameter of 15 mm using laser cutter. Acetone and Milli-Q water were successively applied to wash Kevlar pieces with the assist of ultrasonication. To ensure a good bonding with chemically grown silver layer, an air-plasma treatment was conducted to increase the surface energy of Kevlar fabric which had been dried in an oven at 70ºC for 2 hour. Then pre-treated Kevlar fabrics pieces were sensitized in a solution containing 5 mg ml^{-1} $SnCl_2$ and 0.06 M HCl at room temperature for 1 h under stirring. Milli-Q water was used to thoroughly wash the sensitized fabric before it was subject to the following silver plating process.

The silver plating solution contained 12 mg ml^{-1} $AgNO_3$, 8 mg ml^{-1} NaOH and 6.25 wt% $NH_3{\cdot}H_2O$. The solution of $AgNO_3$ and NaOH produced brown precipitates immediately after the mixing, which disappeared after the addition of $NH_3{\cdot}H_2O$ solution (37%). Then the sensitized Kevlar fabrics were immersed in such sliver plating solution, followed by the quick addition of glucose solution (2.6 mg ml^{-1}) to start the dynamic chemical reaction. The reaction was kept at room temperature for 40 min

 https://doi.org/10.52202/078352-0011

under stirring. The fabric showed a colour change from yellow to metallic silver. After the final rinsing process using acetone and Milli-Q, silver-coated Kevlar fabric were obtained and denoted as Ag-Kevlar.

Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500FA) was applied to investigate the morphology of silver coating. Four-point-probe equipment was used to measure the conductivity.

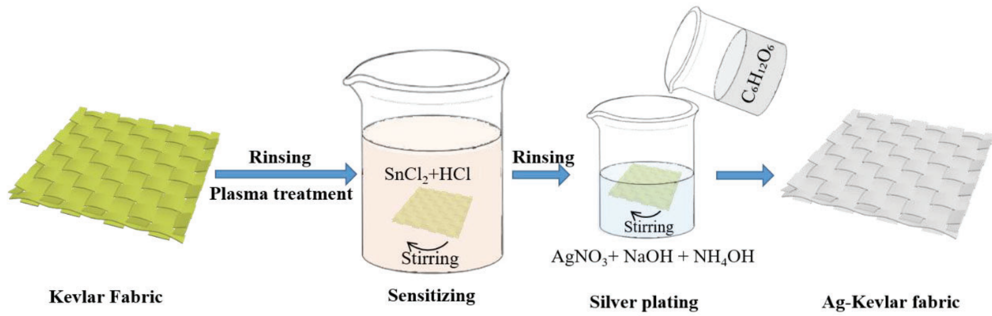

Figure 1. Schematic procedures illustrating the silver plating process on Kevlar fabric.

2.2 Preparation of Ag-Kevlar electrode

Doctor blade technique was used to coat active material slurry onto the conductive Ag-Kevlar substrate. Briefly, graphite/carbon black/PVDF (weight ratio: 8:1:1) in N-Methyl-2-pyrrolidone (NMP) was used as the slurry for anodes. Ag-Kevlar fabric was weighted prior to the coating and after the slurry-coated Ag-Kevlar was dried. The mass difference was used to calculate the weight of coated active material (graphite). The mass loading of graphite was in a range of 2-3 mg cm^{-2}. The Ag-Kevlar anodes were denoted as Ag-Kevlar-G.

2.3 Preparation of STF (shear-thickening fluids) electrolyte

The shear thickening electrolyte were prepared by mixing fume silica particles (SiO_2, S5505, Sigma-Aldrich) in a commercial lithium ion battery electrolyte (Sigma Aldrich), 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC, volume ratio 1:1). SiO_2 particles were first dried in a vacuum oven at 110 ^oC for 24 hours and then kept in the glove box (Oxygen < 1 ppm, H_2O < 1 ppm) for 2 days before the mixing process. Based on previous results [3], 6.3 wt% SiO_2 was added into the commercial electrolyte to function as the shear-thickening electrolyte.

2.4 Electrochemical Measurement

Different combinations of electrodes and electrolyte were assembled into 2032 type coin cell batteries in the glove box (MBrau, UNIlab Plus). The Ag-Kevlar-G anode was used as working electrode with lithium foil as counter electrodes. Two type of electrolyte were used: commercial electrolyte - 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC, volume ratio 1:1), and STF electrolyte. The galvanostatic charge/discharge performance of assembled batteries was investigated using a Neware testing system (Neware Electronic Co.). All the applied current density and obtained specific capacity was calculated based on the mass of active materials in Ag-Kevlar-G anodes.

2.5 Ballistic resistance testing

Ballistic resistance testing was conducted by using a gas gun (8 m). The projectile is Hornady 30 Cal.309 110 GR FML with a mass of 7.1g.

3 RESULTS AND DISCUSSIONS

3.1 Silver coated Kevlar fabric

The morphologies of blank Kevlar fabric and silver-coated Kevlar fabric (Ag-Kevlar) is displayed in Figure 2. After the sliver plating process, pristine Kevlar fabric in yellow color (Figure 2a) was

https://doi.org/10.52202/078352-0011

changed into silvery Ag-Kevlar (Figure 2b). For the sake of uniform Ag coating on Kevlar as well as the accurate mass loading on Ag-Kevlar, a laser cutter machine was used to cut the Kevlar fabric into small round pieces with a diameter of 15 mm (Figure 2c). These type of Kevlar pieces could be directly applied as electrode substrates for use in coin cells. Blank Kevlar fabric were woven with smooth fiber (Figure 2 d-e). After the silver plating process, all fibers were completely covered by silver (Figure f-g). It is also noticed that there were many small silver particle aggregates on the fiber surface, which may lead to increased surface area and has a positive effect on its performance.

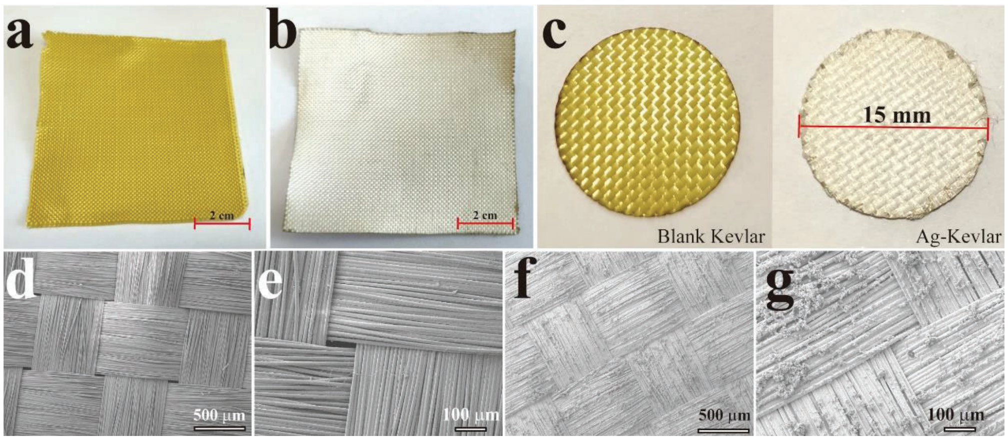

Figure 2. Demonstration of silver-coated Kevlar fabric (Ag-Kevlar). Digital images of large Kevlar fabric before (a) and after silver plating (b); (c) Digital images of the laser-dissected blank Kevlar fabric and silver coated Kevlar (Ag-Kevlar); SEM images showing the surface morphology of (d-e) blank Kevlar fabric and (f-g) Ag-Kevlar at different magnifications.

The properties of blank Kevlar and Ag-Kevlar including density, thickness, conductivity were all investigated, and shown in Table 1. Ag-Kevlar with different silver content were produced for comparison. Sample with low and high mass silver content were denoted as L-Ag-Kevlar and H-Ag-Kevlar respectively. Although Ag-Kevlar samples displayed a higher areal density than the commonly used copper foil (8.7 mg cm^{-2}) in commercial lithium ion batteries, Kevlar fabric with high strength and stress-dispersing weave pattern can well promote the ballistic resistance of batteries. The coated silver layer impacted on the conductivity of Kevlar fabric. The resistance between the double sides of Ag-Kevlar were collected for comparison and named as double-side resistance. With a silver content of 16.5%, the L-Ag-Kevlar presented a double-side resistance in the range of 0.45-0.85 ohm. While the H-Ag-Kevlar with a silver content of 34.7% displayed a high conductivity of 3.78-7.55 S m^{-1}. This good conductivity of the Ag-Kevlar samples demonstrated the potential for used as electrode substrates.

Table 1. Properties of AG-Kevlar fabric.

Sample	Blank Kevlar	L-Ag-Kevlar	H-Ag-Kevlar
Areal density (mg cm^{-2})	12.22	14.63	18.72
Sliver content	0	16.5%	34.7%
Thickness (mm)	0.165	0.182	0.2
Double-side resistance (ohm)	/	0.45-0.85	0.15-0.3
Area (cm^2)	1.766	1.766	1.766
Conductivity (S m^{-1})	/	1.21-2.29	3.78-7.55

To evaluate the performance of the above two type of Ag-Kevlar fabrics, they were all fabricated into electrodes after coating with the graphite slurry. The rate performance and the followed cycling performance with commercial liquid electrolyte are shown in Figure 3a. Clearly, H-Ag-Kevlar displayed excellent rate and cycling performance while L-Ag-Kevlar delivered slightly lower capacity during all the cycles. The discharge capacity for H-Ag-Kevlar-G and L-Ag-Kevlar-G were 547 mAh g^{-1} and 470 mAh g^{-1} at 20 mA g^{-1} (5th cycle), respectively. Even after a cycling test at 20 mA g^{-1}, H-Ag-Kevlar-G delivered a high capacity of ~559 mAh g^{-1} while it was ~500 mAh g^{-1} for L-Ag-Kevlar-G. It is interesting to notice that these two types of electrodes all delivered higher capacity at low current

 https://doi.org/10.52202/078352-0011

density than the theoretical capacity of graphite. Silver can form alloys with lithium ions providing extra capacity as reported[23]. In addition, such fabric electrodes offered large surface area that promoted the diffusion and migration of electrolyte ions into active materials for realizing a high capacity. At a high current density of 100 mA g^{-1}, the discharge capacity was 352 mAh g^{-1} and 240 mAh g^{-1} for H-Ag-Kevlar-G and L-Ag-Kevlar-G electrodes, respectively. The better rate capability of H-Ag-Kevlar-G electrode can be attributed to its higher conductivity.

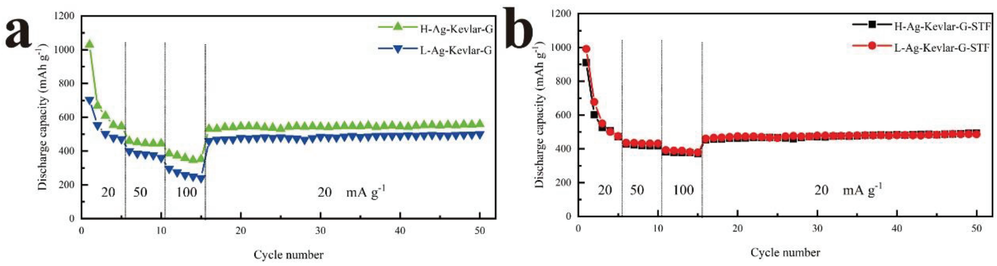

Figure 3. Rate and cycling performance of Ag-Kevlar-G electrodes in a battery system with commercial electrolyte (a) and STF electrolyte (b).

Then soft-amour type battery, Ag-Kevlar-G electrodes in combination with STF electrolyte was assembled, and the electrochemical performance is shown in Figure 3b. H-Ag-Kevlar-G and L-Ag-Kevlar-G electrodes did not show obvious difference regarding to their rate and cycling performance. The capacity for H-Ag-Kevlar-G was 472 mAh g^{-1} at 20 mA g^{-1} (5th cycle), 417 mAh g^{-1} at 50 mA g^{-1} (10th cycle) and 372 mAh g^{-1} at 100 mA g^{-1} (15th cycle); while they were 475 mAh g^{-1}, 432 mAh g^{-1} and 379 mAh g^{-1} for L-Ag-Kevlar-G electrode, respectively. After 35 cycles at 20 mA g^{-1}, both of them delivered a capacity of ~490 mAh g^{-1}, the same range as that battery system with Ag-Kevlar-G anodes and commercial liquid electrolyte. This clearly demonstrates that STF can offer similar function as commercial electrolyte for lithium ion batteries. It also proved that these Ag-Kevlar-G electrodes delivered excellent electrochemical performance in STF electrolyte. It should be pointed out that L-Ag-Kevlar-G electrodes are preferable than H-Ag-Kevlar-G to produce batteries with higher energy density due to its low weight.

3.2 Ballistic resistance testing

Ballistic resistance testing was conducted as shown in Figure 4. As Ag-Kevlar-G electrodes were developed and the electrochemical performances were tested in half cells with lithium foils as counter electrodes. It would most likely cause fire/explosion if performing the ballistic tests with the half cells due to the flammable lithium foil, which become explosive upon the contact with the moisture in air. The ballistic testing were conducted using full cells coupled with Kevlar-based cathodes and the STF electrolyte, the V50 performance of the full cell was 122 m/s. By contrast, the V50 of a full cell with commercial liquid electrolyte and electrode was 77m/s.

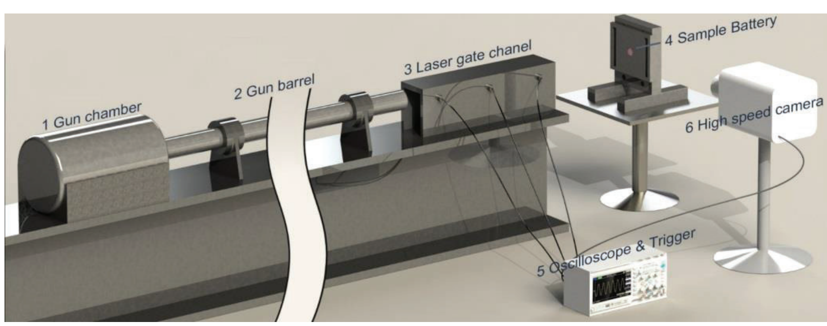

Figure 4. Schematic procedures illustrating the battery ballistic resistance test

4. CONCLUSION

This work intends to develop a ballistic-resistant soft amour battery with Kevlar electrode in combination with a STF electrolyte. With the coating of silver layer through an electroless plating

https://doi.org/10.52202/078352-0011

process, conductive Ag-Kevlar fabric was obtained and displayed low resistance, which is suitable as battery electrode substrate. The amount of sliver coating impacted on the performance of Ag-Kevlar supported graphite (Ag-Kevlar-G) anodes. The Ag-Kevlar-G with high sliver content displayed better performance than that with low sliver content (L-Ag-Kevlar-G) when using commercial liquid electrolyte. They all display stable rate capacity and cycling performance when substituted the commercial electrolyte with STF electrolyte. Take the fabrication of bullet-proof battery into consideration, thin and light L-Ag-Kevlar is preferred as electrode substrates to produce a battery with high energy density. To realize ballistic elbow and knee guards with energy storage capabilities, soft battery system composed of Ag-Kevlar electrodes and STF electrolyte need to be developed. Currently, the research work on Ag-Kevlar cathode is undergoing.

REFERENCES

[1] J. Ding, T. Tian, Q. Meng, Z. Guo, W. Li, P. Zhang, F.T. Ciacchi, J. Huang, W. Yang, Smart multifunctional fluids for lithium ion batteries: Enhanced rate performance and intrinsic mechanical protection, Sci. Rep. 3 (2013) 1–7. doi:10.1038/srep02485.

[2] J. Ding, G. Peng, K. Shu, C. Wang, T. Tian, W. Yang, Y. Zhang, G.G. Wallace, W. Li, Novel reversible and switchable electrolytes based on magneto-rheology, Sci. Rep. 5 (2015) 1–11. doi:10.1038/srep15663.

[3] J. Ding, T. Bussell, C. Wang, K. Shu, Y. Ge, BODY ARMOUR WITH POWER STORAGE CAPABILITIES, n.d.

[4] Y.S. Lee, E.D. Wetzel, N.J. Wagner, The ballistic impact characteristics of Kevlar® woven fabrics impregnated with a colloidal shear thickening fluid, J. Mater. Sci. 38 (2003) 2825–2833. doi:10.1023/A:1024424200221.

[5] E. Haro Albuja, J.A. Szpunar, A.G. Odeshi, Ballistic impact response of laminated hybrid materials made of 5086-H32 aluminum alloy, epoxy and Kevlar® fabrics impregnated with shear thickening fluid, Compos. Part A Appl. Sci. Manuf. 87 (2016) 54–65. doi:10.1016/j.compositesa.2016.04.007.

[6] Y. Park, Y.H. Kim, A.H. Baluch, C.G. Kim, Numerical simulation and empirical comparison of the high velocity impact of STF impregnated Kevlar fabric using friction effects, Compos. Struct. 125 (2015) 520–529. doi:10.1016/j.compstruct.2015.02.041.

[7] A. Haris, H.P. Lee, T.E. Tay, V.B.C. Tan, Shear thickening fluid impregnated ballistic fabric composites for shock wave mitigation, Int. J. Impact Eng. 80 (2015) 143–151. doi:10.1016/j.ijimpeng.2015.02.008.

[8] Q. He, S. Cao, Y. Wang, S. Xuan, P. Wang, X. Gong, Impact resistance of shear thickening fluid/Kevlar composite treated with shear-stiffening gel, Compos. Part A Appl. Sci. Manuf. 106 (2018) 82–90. doi:10.1016/j.compositesa.2017.12.019.

[9] X. Feng, S. Li, Y. Wang, Y. Wang, J. Liu, Effects of different silica particles on quasi-static stab resistant properties of fabrics impregnated with shear thickening fluids, Mater. Des. 64 (2014) 456–461. doi:10.1016/j.matdes.2014.06.060.

[10] S. Gürgen, M.C. Kuşhan, The stab resistance of fabrics impregnated with shear thickening fluids including various particle size of additives, Compos. Part A Appl. Sci. Manuf. 94 (2017) 50–60. doi:10.1016/j.compositesa.2016.12.019.

[11] G. Peng, Y. Ge, J. Ding, C. Wang, G.G. Wallace, W. Li, Magnetorheological technology for fabricating tunable solid electrolyte with enhanced conductivity and mechanical property, Smart Mater. Struct. 27 (2018) 035022. doi:10.1088/1361-665X/AA9F7F.

[12] G.M. Veith, B.L. Armstrong, H. Wang, S. Kalnaus, W.E. Tenhaeff, M.L. Patterson, Shear Thickening Electrolytes for High Impact Resistant Batteries, ACS Energy Lett. 2 (2017) 2084–2088. doi:10.1021/acsenergylett.7b00511.

[13] B.H. Shen, B.L. Armstrong, M. Doucet, L. Heroux, J.F. Browning, M. Agamalian, W.E. Tenhaeff, G.M. Veith, Shear Thickening Electrolyte Built from Sterically Stabilized Colloidal Particles, ACS Appl. Mater. Interfaces. 10 (2018) 9424–9434. doi:10.1021/acsami.7b19441.

[14] B.H. Shen, G.M. Veith, B.L. Armstrong, W.E. Tenhaeff, R.L. Sacci, Predictive Design of Shear-Thickening Electrolytes for Safety Considerations, J. Electrochem. Soc. 164 (2017) A2547–A2551. doi:10.1149/2.1171712jes.

[15] N.J. Wagner, J.F. Brady, Shear thickening in colloidal dispersions, Phys. Today. 62 (2009) 27–32. doi:10.1063/1.3248476.

[16] X. Cheng, J.H. McCoy, J.N. Israelachvili, I. Cohen, Imaging the microscopic structure of shear thinning and thickening colloidal suspensions, Science (80-.). 333 (2011) 1276–1279. doi:10.1126/science.1207032.

[17] S.R. Waitukaitis, H.M. Jaeger, Impact-activated solidification of dense suspensions via dynamic jamming fronts, Nature. 487 (2012) 205–209. doi:10.1038/nature11187.

[18] X. Wu, F. Zhong, Q. Yin, C. Huang, Dynamic response of shear thickening fluid under laser induced shock, Appl. Phys. Lett. 106 (2015) 071903. doi:10.1063/1.4913423.

[19] J. Yang, S. Sun, W. Li, H. Du, G. Alici, M. Nakano, Development of a linear damper working with magnetorheological shear thickening fluids, J. Intell. Mater. Syst. Struct. 26 (2015) 1811–1817. doi:10.1177/1045389X15577653.

[20] S.Q. Jiang, E. Newton, C.W.M. Yuen, C.W. Kan, Chemical silver plating and its application to textile fabric design, J. Appl. Polym. Sci. 96 (2005) 919–926. doi:10.1002/app.21541.

https://doi.org/10.52202/078352-0011

[21] Snouqiang Jiang, E. Newton, C.-W. Marcus Yuen, C.-W. Kan, Application of Chemical Silver Plating on Polyester and Cotton Blended Fabric, Text. Res. J. 77 (2007) 85–91. doi:10.1177/0040517507078739.

[22] C.W.M. Yuen, S.X. Jiang, C.W. Kan, S.K.A. Ku, P.S.R. Choi, K.P.M. Tang, S.Y. Cheng, Polyester Metallisation with Electroless Silver Plating Process, Fibers Polym. 14 (2013) 82–88. doi:10.1007/s12221-013-0082-y.

[23] M.N. Obrovac, V.L. Chevrier, Alloy Negative Electrodes for Li-Ion Batteries, Chem. Rev. 114 (2014) 11444−11502. doi:10.1021/cr500207g.

https://doi.org/10.52202/078352-0011